

THE CONDUCTIVITY AND VISCOSITY
OF SOLUTIONS OF CERTAIN SALTS
IN WATER, METHYL ALCOHOL,
ETHYL ALCOHOL, ACETONE

AND BINARY MIXTURES OF THESE SOLVENTS

BY

W. R. VEAZEY

DISSERTATION

*Submitted to the Board of University Studies of the Johns Hopkins
University in Conformity with the Requirements for the
Degree of Doctor of Philosophy*

1907

THE CONDUCTIVITY AND VISCOSITY
OF SOLUTIONS OF CERTAIN SALTS
IN WATER, METHYL ALCOHOL,
ETHYL ALCOHOL, ACETONE

AND BINARY MIXTURES OF THESE SOLVENTS

BY

W. R. VEAZEY



DISSERTATION

*Submitted to the Board of University Studies of the Johns Hopkins
University in Conformity with the Requirements for the
Degree of Doctor of Philosophy*

1907



Digitized by the Internet Archive
in 2026

ACKNOWLEDGMENT.

To President Remsen, Professor Morse, and Professor Jones I desire to express my most sincere gratitude for the instruction and advice given me by them throughout my entire course in both lecture room and laboratory.

I desire also to thank Professor Hulburt, Dr. Gilpin, Dr. Tingle, and Dr. Acree for instruction received from them.

This investigation was begun at the suggestion of Professor Jones, and was carried out under his direction.

CONTENTS.

ACKNOWLEDGMENT	PAGE iii
--------------------------	-------------

PART I.

INTRODUCTION	v
------------------------	---

PART II.

EXPERIMENTAL :

(a) Conductivity	1
(b) Viscosity	2
Solvents	3
Solutions	4
CONDUCTIVITY MEASUREMENTS	4
Copper Chloride	5
Potassium Sulphocyanate	12
VISCOSITY MEASUREMENTS	24
SUMMARY OF FACTS ESTABLISHED	33

PART III.

DISCUSSION OF RESULTS	38
SUMMARY	47
BIOGRAPHY	51

PART I.

INTRODUCTION.

A COMPLETE historical reference to the literature connected with this subject has already been given by Jones and his co-workers.¹ It is desirable, therefore, at the beginning of this investigation to give simply a general summary of the six pieces of work already done in this field, and the conclusions which have been drawn from them.

The work of *Jones and Lindsay*² included the following solvents: water, methyl alcohol, ethyl alcohol, and propyl alcohol, and mixtures of these solvents with one another. The electrolytes which they dissolved in these solvents are potassium iodide, ammonium bromide, strontium iodide, cadmium iodide, lithium nitrate, and ferric chloride.

A minimum in the molecular conductivity was found for all the salts studied in mixtures of methyl alcohol and water, with the exception of cadmium iodide. A minimum was also found in the mixtures of ethyl alcohol and water, especially at zero degrees; the minimum disappearing at twenty-five degrees. Mixtures of methyl alcohol with ethyl alcohol do not show the minimum in the conductivity, but in the 50 per cent mixture of these solvents the molecular conductivity of dissolved electrolytes is less than the mean of the conductivities of the separate solvents. The explanation that was offered by Jones and Lindsay to account for the conductivity minimum in the mixed solvents, is that in these associated solvents each solvent diminishes the association of the other. Since the dissociating power is a function of the association of the solvent, anything which will diminish the association will diminish the dissociating power. The effect of mixing two dissociating solvents would thus be to diminish the association of both, and, consequently, the dissociating power of each of the solvents. A mixture of two such solvents would, then, dissociate less than either alone, and the conductivity of an electrolyte in such a mixture would be less than in the individual solvents — the conductivity curve would pass through a minimum.

This explanation would account for the conductivity minimum in the mixed solvents. The fundamental question, however, is: Is this explanation true?

¹ Amer. Chem. Journ., **28**, 329 (1902); **32**, 521 (1904); **34**, 481 (1905); **36**, 325 (1906).

² Amer. Chem. Journ., **28**, 329 (1902).

There is considerable experimental evidence bearing upon this question. The molecular weights of the alcohols when dissolved in water are, in general, normal, *i.e.*, the molecules of the alcohols are the simplest possible. In pure alcohols, however, the molecules are quite complex, as is shown by the surface tension method of Ramsay and Shields.¹ The water has thus broken down the complex molecules of alcohol into simpler molecules.

A more direct line of evidence bearing upon this problem has been furnished by the work of *Jones and Murray*.² They worked with mixtures of water, formic acid, and acetic acid, with each other. It will be recognized that these are all associated liquids. The molecular weight of each of these liquids dissolved in each of the other two was determined by the freezing-point method. It was found that the molecular weight was smaller the more dilute the solution, and even in the most concentrated solutions which could be studied, the molecular weight was always much less than the molecular weight of the substance when in the pure homogeneous condition. This showed beyond question that the action of an associated liquid is to diminish the association of another associated liquid.

The above explanation to account for the conductivity minimum in the mixed solvents is then undoubtedly an important factor.

The investigation by *Jones and Carroll*³ included the same solvents that had been used by Jones and Lindsay, *i.e.*, water, methyl alcohol, ethyl alcohol, and binary mixtures of these solvents; and in addition acetic acid was also used. The electrolytes employed by Carroll are: cadmium iodide, sodium iodide, calcium nitrate, hydrochloric acid, and sodium acetate in mixtures of acetic acid and water.

The minimum in the molecular conductivity was found for cadmium iodide, sodium iodide, and hydrochloric acid, in mixtures of methyl alcohol and water. The dissociation of sodium iodide, potassium iodide, and potassium bromide in a 50 per cent mixture of methyl alcohol and water was directly determined, and was found to be apparently slightly greater than in water alone at the same dilution.

The question as to the cause of the minimum in conductivity was then taken up. It was shown that there is a parallelism between the conductivity minimum and the minimum in the fluidity of the solvent. It was further shown that both minima are more pronounced at lower temperatures, and that both occur at approximately the same points. Again, the effect of rise in temperature is the same upon both minima, *i.e.*, a shift toward the mixture containing the greater per cent of alcohol.

From a quantitative study of these two classes of phenomena the con-

¹ Ztschr. phys. Chem., **12**, 433 (1893).

³ Ibid., **32**, 521 (1904).

² Amer. Chem. Journ., **30**, 193 (1903).

clusion was drawn that the decrease in conductivity of electrolytes when dissolved in binary mixtures of various alcohols and water, which is frequently accompanied by a well-defined minimum in conductivity, is largely due to the diminution in the fluidity of the solvent which takes place when the two solvents are mixed. This diminishes the velocity with which the ions move, and, consequently, diminishes the conductivity.

A quantitative comparison was then made of the conductivity of the different solvents with their viscosities. In order that this comparison can be made for different solvents we must deal with "comparable equivalent solutions," *i. e.*, solutions containing the same number of gram-molecules of electrolyte in the same number of gram-molecules of the different solvents.

The result was to show that conductivities of "comparable equivalent solutions" of binary electrolytes in such solvents as members of the methyl alcohol series, acetone, etc., are inversely proportional to the coefficient of viscosity of the solvent in question, and directly proportional to the association factor of the solvent, or to the amount of the dissociation of the substance dissolved in that solvent.

This is essentially the same as to say that the hypothesis of Dutoit and Aston holds quantitatively for certain electrolytes, in such solvents as water, methyl alcohol, and ethyl alcohol.

While the larger part of the work of *Jones and Bassett*¹ had to do with the question of the relative velocities of the ions of silver nitrate in non-aqueous solvents, and in mixtures of these solvents with water and with one another, yet they took up the problem of the conductivity of silver nitrate in water, in methyl alcohol, in ethyl alcohol, and in binary mixtures of these solvents with one another.

It was shown that silver nitrate in mixtures of methyl alcohol and water give a minimum in conductivity at both zero degrees and twenty-five degrees. Silver nitrate, however, in mixtures of ethyl alcohol and water does not show the minimum at either zero degrees or twenty-five degrees.

When the conductivities at zero degrees are compared with those at twenty-five degrees, we see that the influence of one solvent on the other is greater the lower the temperature.

This is exactly what would be expected in terms of the suggestion put forward in the work of Jones and Lindsay.² As the temperature is raised the association of the associated solvents becomes less and less; consequently each solvent will diminish the association of the other less and less as the temperature becomes higher and higher.

The investigation carried out by *Jones and Bingham*³ included the sol-

¹ Amer. Chem. Journ., **32**, 409 (1904).

³ Ibid., **34**, 481 (1905).

² Ibid., **28**, 329 (1902).

vents used in the earlier work — water, methyl and ethyl alcohols, and in addition acetone was employed. The conductivities of lithium nitrate, potassium iodide, and calcium nitrate in these solvents, and in binary mixtures of one with another, were measured. In this investigation a fairly large number of viscosity measurements were also made. These included not simply the measurement of the viscosities of the pure solvents and of mixtures of these with one another, but also the viscosities of solutions of calcium nitrate in the different solvents and in the mixtures of these with one another. The temperature coefficients of conductivity and of fluidity in mixtures of acetone with the other solvents were also compared.

The conductivities in mixtures of acetone with water show the minimum previously observed in a number of cases. This minimum is closely connected with the minimum in fluidity observed in these mixtures.

The conductivities of potassium iodide in mixtures of methyl or ethyl alcohol with acetone obey the rule of averages, and the conductivity curves are nearly straight lines at all the dilutions. In mixtures of acetone with the alcohols the fluidity curve is nearly a straight line.

One of the most important facts brought out in this investigation, and one that had not been observed in any of the previous work, is that lithium nitrate and calcium nitrate give a very pronounced maximum in conductivity in mixtures of acetone with methyl alcohol or ethyl alcohol. It was pointed out that this must be due either to an increase in the dissociation increasing the number of ions present, or to a diminution in the size of the ionic spheres causing the ions present to move more rapidly.

It was shown possible to eliminate one of these.

The fluidities of mixtures of acetone with the alcohols were shown to obey the rule of averages, which would indicate that there is no increase in the molecular aggregation when the alcohols and acetone are mixed. In terms of the well-established hypothesis of Dutoit and Aston, such a mixture would not dissociate to a greater extent than the constituent solvents. Further, direct measurements of dissociation at extreme dilutions have failed to show any great difference between the dissociating power of the mixtures and that of the pure solvents. Further, the maximum moves from the 25 per cent mixture at large concentration to the 75 per cent mixture in the more dilute solutions. This would not be expected if the dissociating power is greatest in a certain mixture.

We have thus eliminated the increase in dissociation as being the cause of the maximum and are compelled to accept the other alternative, that the maximum in conductivity is due to a change in the dimensions of the atmospheres about the ions.

In dealing with conductivity in single solvents, and in mixtures of these with one another, we must take into account not only the effect of each

constituent of the mixture on the association of all the other constituents, and the viscosity of the individual solvent or solvents, but also the sizes of the spheres of the solvents around the ions, and any changes in the sizes of these spheres in different mixtures of the solvents.

These ionic spheres or solvates have been shown by Jones ¹ to exist generally in solutions, and the ions must drag these spheres with them in their movements under the action of a current.

Any change in the size of these spheres would produce a change in the effective mass of the ion, and, consequently, a change in the velocity with which it would move.

It was also shown that the hyperbola and not the straight line is the normal curve of viscosity.

While the work of *Jones and Rouiller* ² had to do more especially with the velocities of ions in mixed solvents, yet he studied the conductivities of silver nitrate in acetone, in mixtures of acetone with water, in mixtures of methyl alcohol and ethyl alcohol, in methyl alcohol and acetone, and in ethyl alcohol and acetone.

Silver nitrate in mixtures of methyl alcohol and acetone and ethyl alcohol and acetone shows a pronounced maximum in conductivity, strictly analogous to calcium nitrate, which has been studied in these solvents by Jones and Bingham. ³

The work of Jones and Rouiller on the migration velocity of ions in mixtures of these solvents would indicate that the explanation of the conductivity maximum offered by Jones and Bingham is correct — there is a change in the size of the atmosphere of the solvent about the ions.

The investigation of *Jones and McMaster* ⁴ included the same solvents that had been used by Bingham, — water, methyl alcohol, ethyl alcohol, and acetone, and binary mixtures of these solvents. The electrolytes used were lithium bromide and cobalt chloride. The conductivities of a large number of solutions of these substances in the above solvents and in binary mixtures of these solvents were measured.

The fluidities of water, methyl alcohol, ethyl alcohol, and acetone, and binary mixtures of these solvents, were measured. The conductivities in mixtures of the alcohols with water, and in the mixtures of acetone with water, show a well-marked minimum. This minimum in conductivity is more pronounced at the lower temperature, and is intimately connected with the minimum in fluidity observed in the above mixtures.

The conductivity curves in mixtures of methyl and ethyl alcohols are

¹ Carnegie Institution of Washington,
Publication No. 60.

² Amer. Chem. Journ., **36**, 427 (1906).

³ Ibid., **34**, 481 (1905).

⁴ Ibid., **36**, 325 (1906).

nearly straight lines, obeying the law of averages, as would be expected. Lithium bromide dissolved in mixtures of methyl or ethyl alcohol with acetone shows a pronounced maximum in conductivity. The conductivity maximum is also given by cobalt chloride in mixtures of acetone with ethyl alcohol.

The fluidities of lithium bromide in mixtures of acetone with the alcohols were found to be what would be expected from the rule of averages, — the fluidity curves being nearly straight lines. The same was found for the pure solvents. This would indicate that the alcohols and acetone do not form more complex aggregations when mixed than when alone.

Jones and McMaster, therefore, arrive at the same conclusion as that reached by Jones and Bingham, *i.e.*, that the size of the ionic spheres is an important factor in determining conductivity, and that changes in the sizes of these spheres in different mixtures of the solvents are the prime factor in conditioning the maximum in the conductivity curve.

Some interesting results were obtained in this investigation bearing on the temperature coefficients of conductivity.

Jones¹ has recently pointed out the bearing of hydrates on the temperature coefficients of conductivity. *Jones and West*² showed that with rise in temperature there is a decrease in the dissociation, and that increase in conductivity with rise in temperature is due primarily to an increase in the velocities with which the ions move. As the temperature is raised the hydrates in combination with the ion become simpler and simpler, and, therefore, the effective mass of the ion decreases with rise in temperature. The ion being smaller and the solvent less viscous, it will move faster the higher the temperature.

Jones has also pointed out in terms of his hydrate theory that the greater the dilution the greater should be the temperature coefficient of conductivity. The more dilute the solution, the more complex the hydrate; the more complex the hydrate in combination with any given ion, the greater the change in the complexity of the hydrate with rise in temperature. The temperature coefficient of conductivity should, therefore, be greater in the more dilute solution, and such is the fact. The work of Jones and McMaster showed that the temperature coefficients of conductivity and of fluidity for lithium bromide are of the same order of magnitude, — the temperature coefficients for this substance in the mixed solvents all being positive.

In certain of the mixtures of acetone with the alcohols cobalt chloride showed negative temperature coefficients of conductivity. This was true in the 75 per cent mixture of acetone with methyl alcohol and also in the 50 per cent

¹ Carnegie Institution of Washington,
Publication No. 60.

² Amer. Chem. Journ., **34**, 357 (1905).

and 75 per cent mixtures of acetone with ethyl alcohol. Negative temperature coefficients had previously been found in a few cases at low temperatures, but in this work negative temperature coefficients were found at ordinary temperatures.

The meaning of *negative temperature coefficients* of conductivity according to Jones and McMaster is as follows: With rise in temperature the solvent becomes less viscous and this would increase the velocity of the ions. With rise in temperature, however, the association of the solvent becomes less, and, consequently, its dissociating power is diminished; which means that there would be a smaller number of ions present the higher the temperature. These two influences act counter to one another, the former increasing the conductivity and the latter diminishing it.

When we have negative temperature coefficients of conductivity, it means that the latter influence more than overcomes the former — the decrease in the number of ions with rise in temperature more than counterbalances the effect of the increased velocity with which the ions move. The result is a decrease in conductivity with rise in temperature.

The alcohols and acetone are at ordinary temperatures associated liquids. The effect of rise in temperature is to diminish their association and hence their dissociating power.

EXPERIMENTAL.

APPARATUS.

CONDUCTIVITY.

THE conductivity measurements were made by the Kohlrausch method, using a Wheatstone bridge, induction coil, and telephone receiver.

The bridge-wire, which was of "manganin," was carefully calibrated by the method of Strouhal and Barus,¹ and was found to have practically uniform resistance throughout its entire length.

All readings were taken within 100 mm. of either side of the center of the wire.

The resistance coils were made by Leeds & Co. and were accurate to within 0.04 per cent.

The conductivity cells were those used by Jones and Bingham² and by Jones and McMaster.³ These cells were found to be very satisfactory. The cell constants in no case varied more than one unit in twelve months' continual use.

The zero-bath was prepared in the following manner: A porcelain enameled bucket, of about $1\frac{1}{2}$ gallons capacity, was filled with finely crushed ice moistened with pure water. This vessel was placed in a fibroid bucket of 3 gallons capacity, the intervening space between the two being filled with ice and water as above described.

The bath thus prepared was found, when tested with a standard thermometer, to vary from the desired temperature not more than 0.05° , and to remain practically constant for at least 5 hours.

The 25° bath consisted of a round galvanized-iron vessel, of about 20 liters capacity, filled with water. The bath was stirred by means of a small propeller, driven by a Heinrich hot-air motor.

The thermometers used were graduated to 0.2° , and were carefully standardized by comparison with a thermometer which was tested at the "Reichsanstalt."

All burettes and flasks used in the preparation of solutions were carefully calibrated at 20° .

¹ Wied. Ann., **10**, 326 (1880).

² Ibid., **36**, 331 (1906).

³ Amer. Chem. Journ., **34**, 493 (1905).

VISCOSITY.

The viscometer used was a modified form of the one described by Ostwald and Luther.¹ The form described by them was found to be unsatisfactory for liquids having a much greater viscosity than water. The most serious objections are:

(1) The small capillary, above and below the bulb, renders it impossible to make an accurate observation of the meniscus of the descending column of liquid as it passes the mark.

(2) In case a liquid more viscous than water is used, the small capillary invariably fails to drain perfectly, and the liquid bridges over the capillary just above the bulb, thus forming a sort of valve which renders the results of the measurement entirely inaccurate.

To overcome these difficulties the following modified form was made: A large capillary was placed above and below the bulb, and the small capillary was joined to it as shown in fig. 78. The upper bulb of the viscometer had a capacity of about 3 c. c., and the lower bulb a capacity of about 5 c. c. The liquid was raised from the lower to the upper bulb by means of an aspirating bottle, the air being dried over soda-lime. The time of flow through the capillary tube was determined by means of a stop-watch reading to fifths of a second. The stop-watch used was found to be accurate to one-fifth of a second. This was established by a number of comparative tests with other standard watches.



FIG. 78.

The specific gravity of the solution is needed in the calculation of its viscosity. For specific-gravity measurements a slightly modified form of the pycnometer employed by Jones and Bingham² was used. This form of pycnometer is shown in fig. 79. The modification consists in the elongation of the large bulb, which brings a larger surface of the pycnometer, per unit volume, in contact with the bath. The small bulb was made oval in shape so as to secure a better draining of the bulb, and the whole instrument was of much lighter construction and of somewhat greater capacity than that employed by Jones and Bingham.

The zero-bath consisted of a large glass cylinder filled with crushed ice moistened with water. It was found necessary to have the viscometer

¹ Amer. Chem. Journ., 16, 479 (1894).

² Ibid., 34, 495 (1905).

placed at least 2 or 3 cm. from the walls of the bath, to insure uniform temperature; and to render the graduations on the viscometer more clearly visible they were filled with India ink, which was then rendered insoluble by heating. The thermometer bulb was always placed *between the bulb of the viscometer and the wall of the bath*, in order to make certain that that portion of the bath was at the proper temperature. This precaution is necessary, since it was determined by a number of experiments that if any very large amount of water is allowed to collect next to the wall of the bath, its temperature may rise as much as one-half a degree above zero. With a little care, however, it was found possible to keep the portion of the bath immediately surrounding the viscometer constant to within less than one-tenth of one degree.

The 25° bath was similar to that described by Jones and McMaster.¹ It was found desirable to place a small quantity of potassium dichromate in this bath, since this not only prevented the accumulation of organic growth in the bath, but also the yellow color made the graduations on the instrument placed in the bath much more clearly visible. This bath was easily maintained constant to within one-tenth of a degree, by means of a small flame regulated by a Mohr pinchcock.

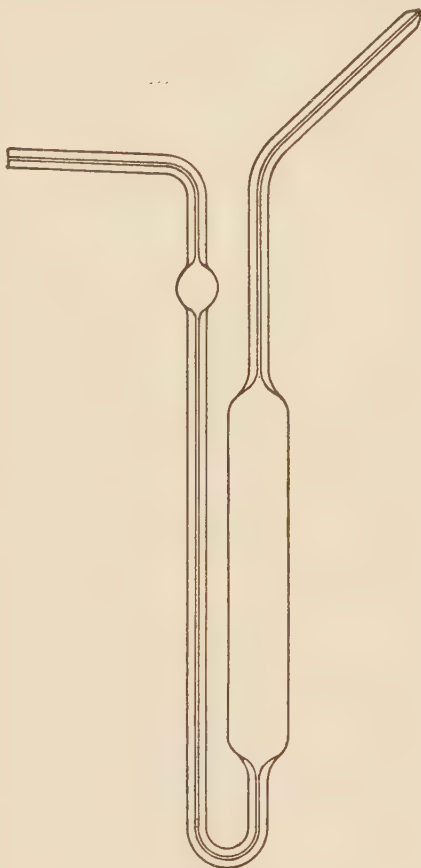


FIG. 79.

SOLVENTS.

WATER.

The water used was purified as follows: Ordinary distilled water was distilled from potassium dichromate and sulphuric acid. It was then distilled a second time from potassium dichromate and sulphuric acid, into barium hydroxide, from which it was finally distilled into a bottle which was protected from the carbon dioxide of the air and other impurities, by a tube filled

¹ Amer. Chem. Journ., **36**, 333 (1906).

with soda-lime. Water purified in this manner had a conductivity of from 1×10^{-6} to 1.5×10^{-6} at 0° , and from 1.8×10^{-6} to 2.5×10^{-6} at 25° .

METHYL ALCOHOL.

The methyl alcohol used was the best that could be obtained commercially. It was purified by boiling over calcium oxide for several days, and then distilled into a glass-stoppered bottle containing anhydrous copper sulphate, where it was allowed to stand for at least a month before using. To prepare the alcohol for final use, it was distilled from the copper sulphate into a bottle carefully protected from moisture, the first and last 150 c.c. of the distillate being discarded. The conductivity of the methyl alcohol thus prepared was practically the same as that of the water.*

ETHYL ALCOHOL.

The ethyl alcohol was purified in the same manner as the methyl alcohol, and gave an average value for conductivity of from 2×10^{-7} to 3×10^{-7} at 0° , and from 5×10^{-7} to 7×10^{-7} at 25° .

ACETONE.

The acetone was dried over fused calcium chloride for about one month, and then distilled immediately before using, in the same manner as the alcohol. Its average conductivity was about 3×10^{-7} at 0° , and 4×10^{-7} at 25° .

SOLUTIONS.

In making up the mixed solvents and in diluting the solutions to any given volume, care was taken to bring all solvents and solutions to exactly 20° before making the measurements or dilutions. In all cases when one solvent was mixed with another, or a salt was dissolved in a solvent, the solution was brought to 20° before making up to the complete volume. The mixed solvents were made up as designated by Jones and Bingham,¹ *i. e.*, " x c. c. of acetone diluted to 100 c. c. was designated as a mixture of x per cent acetone."

The mother-solutions were prepared by weighing the salt directly into the measuring flask and diluting with the solvent to a known volume. From this mother-solution the other solutions were prepared by dilution to the desired volume. Whenever this would require the use of less than 5 c. c. of the mother-solution, a more dilute mother-solution was prepared, and from this the successive dilutions were made.

CONDUCTIVITY MEASUREMENTS.

Four readings were taken with each solution, using a different resistance for each reading. The cell constants were determined in the usual way by

¹ Amer. Chem. Journ., **34**, 494 (1905).

the use of N/50 and N/500 solutions of potassium chloride. The value used for N/50 potassium chloride at 25° was 129.7. The value for N/500 potassium chloride was determined every time a fresh solution of it was prepared, by first determining the cell constants of several cells with N/50 potassium chloride, and then using these cells to determine the value for N/500 potassium chloride. The cell constants were checked at frequent intervals. After use the cells were repeatedly rinsed with distilled water, and when not in use the cells were filled with distilled water. The cells before use were rinsed with water and then with absolute alcohol, and allowed to dry at ordinary temperatures.

The use of ether in drying the cells was avoided, since it is likely to contain small amounts of non-volatile substances.

In table 78 v is the number of liters of solvent that contain 1 gram-molecular weight of the salt; $\mu_v 0^\circ$ is the molecular conductivity at 0°, and $\mu_v 25^\circ$ is the molecular conductivity at 25°.

The temperature coefficients were calculated according to the Kohlrausch formula, and, if multiplied by 100, would express the temperature coefficients in percentage of conductivity units. The Kohlrausch formula as it was applied is
$$\frac{\mu_v 25^\circ - \mu_v 0^\circ}{25} \cdot \frac{1}{\mu_v 0^\circ}$$

COBALT NITRATE.

A number of methods were used in an attempt to obtain perfectly anhydrous cobalt nitrate, but without success; and since it is absolutely necessary to have the salt completely anhydrous for this work, this salt had to be abandoned.

The most nearly successful attempt to dehydrate the salt was carried out as follows: The salt was heated several days to dryness on a water-bath, and was then recrystallized several times from strong nitric acid. The crystals were then washed with anhydrous ligroine to free them from the acid. They were then filtered and drained by the aid of a suction-pump, the funnel containing the crystals being carefully protected from the moisture of the air. The salt was then heated for a day or two in a current of dry air at a temperature of from 50° to 60°. An analysis of the sample thus obtained, for metallic cobalt by the electrolytic method, showed that the salt still contained a considerable amount of water.

COPPER CHLORIDE.

The copper chloride used in this work was prepared as follows: Kahlbaum's pure crystallized copper chloride was recrystallized from dilute hydrochloric acid to free it from small quantities of basic salt. These crystals were then

dehydrated by heating in a current of dry hydrochloric acid, at a temperature of from 140° to 150° , to constant weight. The salt was then placed in a vacuum desiccator over sulphuric acid and potassium hydroxide, to remove any traces of hydrochloric acid. The salt had a dark-brown color, and gave perfectly clear solutions when dissolved in the water or the alcohols. The salt was analyzed by the electrolytic method, using a rotating anode. The results of the analysis agreed with the calculated result for pure copper chloride to within 0.05 per cent. The salt was preserved in glass-stoppered bottles over phosphorus pentoxide.

The results obtained in the mixture of methyl alcohol and water were not entirely satisfactory, because of the formation in the 50 per cent, and more especially in the 75 per cent mixtures, of a cloudiness in the solutions within a few minutes after dissolving the salt. This was probably due to a partial reduction of the salt by the alcohol in the presence of water, since no such action could be observed in either the methyl alcohol or the aqueous solutions. The conductivity of the solutions in which the cloudiness appeared was determined without filtering the solution, and after 24 hours the conductivity of the solution was again determined. No appreciable change in the conductivity could be detected, showing that the change in the solution proceeded rapidly at first and soon reached the equilibrium point.

An attempt was made to determine the conductivity of copper chloride in acetone, and mixtures of acetone with other solvents, but there was a very appreciable action between the salt and the acetone, and, consequently, work in this field was given up. There was not only a very rapid change in the conductivity of the acetone solutions of copper chloride, so that it was impossible to duplicate results; but the molecular conductivity varied with the dilution in a peculiar manner — becoming greater with increase in dilution from $N/100$ to $N/200$, and then decreasing from $N/200$ to $N/800$, where the values reached a minimum, and then increasing again from $N/800$ to $N/1600$.

The solutions changed color slowly on standing for some time, and when the solvent was distilled off on a water-bath apparently an organo-metallic compound remained in the flask, which had none of the properties of either cupric or cuprous chloride.

Table 78, for copper chloride, in mixtures of methyl alcohol and water, when plotted as curves (figs. 80 and 81), shows that there is a decided drop in the curves below the rule of averages, and that this drop in the curve is most pronounced in the 50 per cent mixtures. The values between 75 per cent and 100 per cent mixtures are practically in accord with the rule of averages, at 25° , and have a general tendency in the same direction at 0° .

It is also to be observed that the values for the conductivity in methyl alcohol are very much smaller than the corresponding values in water.

COPPER CHLORIDE.

7

TABLE 78. — *Conductivity of copper chloride at 0° and 25°.*

ν	In water.			In 25 p. ct. methyl alcohol and water.			In 50 p. ct. methyl alcohol and water.		
	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temp. coef.	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temp. coef.	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temp. coef.
10	89.28	162.60	0.03285	48.12	98.73	0.0421	35.35	68.27	0.0372
50	103.94	193.87	.03461	56.57	119.03	.0442	43.92	88.14	.0403
100	106.14	204.86	.03720	59.96	128.00	.0454	46.99	95.63	.0414
200	115.03	214.87	.03471	52.14	133.80	.0461	50.14	102.24	.0416
400	117.47	220.34	.03503	65.36	141.60	.0467	53.22	110.48	.0430
800	123.73	231.03	.03469	67.45	146.90	.0471	54.91	114.56	.0435
1600	129.52	249.70	.03712	67.37	147.30	.0475	59.01	123.50	.0437

ν	In 75 p. ct. methyl alcohol and water.			In methyl alcohol.			In 25 p. ct. ethyl alcohol and water.		
	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temp. coef.	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temp. coef.	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temp. coef.
10	30.28	48.20	0.0237	15.04	17.98	0.00984	34.45	81.17	0.0543
50	42.17	69.75	.0262	27.28	32.98	.00936	40.50	99.17	.0578
100	47.95	80.59	.0272	33.58	42.37	.01047	43.27	107.01	.0589
200	52.48	89.97	.0286	40.46	50.06	.00949	45.12	112.44	.0597
400	57.06	99.83	.0300	46.36	57.78	.00985	46.31	116.73	.0608
800	59.87	106.13	.0309	53.51	65.78	.00917	47.45	119.85	.0610
1600	63.67	114.25	.0318	60.25	72.64	.00823	49.06	126.90	.0635

ν	In 50 p. ct. ethyl alcohol and water.			In 75 p. ct. ethyl alcohol and water.			In ethyl alcohol.		
	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temp. coef.	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temp. coef.	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temp. coef.
10	19.66	46.98	0.0556	13.24	25.17	0.0360	3.53	4.88	0.0153
50	24.41	61.24	.0604	18.64	36.83	.0390	6.42	8.30	.0117
100	26.60	67.56	.0616	21.20	42.46	.0401	8.48	12.07	.0169
200	28.28	73.05	.0633	24.17	48.81	.0408	10.20	13.59	.0133
400	29.79	77.84	.0645	26.33	53.92	.0419	12.01	17.18	.0172
800	30.87	81.43	.0655	28.25	59.05	.0436	13.95	19.92	.0171
1600	32.57	88.16	.0683	32.36	67.31	.0432	15.91	25.24	.0235

ν	In 25 p. ct. methyl alcohol and ethyl alcohol.			In 50 p. ct. methyl alcohol and ethyl alcohol.		
	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temperature coefficient.	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temperature coefficient.
10	5.12	6.39	0.00992	7.81	0.57	0.00901
50	9.63	11.83	.00914	14.68	18.09	.00929
100	12.35	15.48	.01014	18.43	23.21	.01037
200	15.16	17.47	.00610	22.39	28.94	.01170
400	18.17	24.18	.01320	26.54	35.54	.01356
800	20.76	28.58	.01510	29.77	40.70	.01469
1600	23.97	34.90	.01830	34.83	48.90	.01616

ν	In 75 p. ct. methyl alcohol and ethyl alcohol.			In ethyl alcohol and water.				
	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temp. coef.	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.
10	11.44	13.88	0.00853	0.0329	0.0543	0.0556	0.0360	0.0153
50	21.10	25.93	.00916	.0346	.0578	.0604	.0390	.0117
100	26.08	32.61	.01002	.0372	.0589	.0616	.0401	.0169
200	31.28	39.98	.01113	.0347	.0597	.0633	.0408	.0133
400	37.33	48.80	.01229	.0350	.0608	.0645	.0419	.0172
800	40.95	53.75	.01250	.0347	.0610	.0655	.0436	.0171
1600	48.76	64.12	.01260	.0371	.0635	.0683	.0432	.0235

In studying the temperature coefficients of conductivity, it is to be noted that in every case, with the exception of pure methyl alcohol, there is an increase in the temperature coefficient with increase in dilution. This increase, although not perfectly regular, is, however, decidedly marked when the difference in the value for the most concentrated and for the most dilute solution is considered. It is also to be observed that the temperature coefficients in the 25 per cent mixture are decidedly larger than the corresponding values in either of the other mixtures used.

TABLE 79. — *Comparison of the conductivities of copper chloride.*

<i>v</i>	In mixtures of methyl alcohol and water at 0°.					In mixtures of methyl alcohol and water at 25°.				
	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.
10	89.28	48.12	35.35	30.28	15.04	162.60	98.73	68.27	48.20	17.98
50	103.94	56.57	43.92	42.07	27.28	193.87	119.03	88.14	69.75	32.98
100	106.14	59.96	46.99	47.95	33.58	204.86	128.00	95.63	80.59	42.37
200	115.03	62.14	50.14	52.48	40.46	214.84	133.80	102.24	89.97	50.06
400	117.47	65.36	53.22	57.06	46.36	220.34	141.60	110.48	99.82	57.78
800	123.73	67.45	54.91	59.87	53.51	231.03	146.90	114.56	106.13	65.78
1600	129.52	67.37	59.01	63.61	60.25	249.70	147.30	123.50	114.25	72.64

<i>v</i>	In mixtures of ethyl alcohol and water at 0°.					In mixtures of ethyl alcohol and water at 25°.				
	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.
10	89.28	34.45	19.66	13.24	3.53	162.60	81.17	46.98	25.17	4.88
50	103.98	40.50	24.41	18.64	6.42	193.87	99.17	61.24	36.83	8.30
100	106.14	43.27	26.60	21.20	8.48	204.86	107.01	67.56	42.46	12.07
200	115.03	45.12	28.28	24.17	10.20	214.84	112.44	73.05	48.81	13.59
400	117.47	46.31	29.79	26.33	12.01	220.34	116.73	77.84	53.92	17.18
800	123.73	47.45	30.87	28.25	13.95	231.03	119.85	81.43	59.05	19.92
1600	129.52	49.06	32.57	32.36	15.91	249.70	126.90	88.16	67.31	25.24

<i>v</i>	In mixtures of methyl alcohol and ethyl alcohol at 0°.					In mixtures of methyl alcohol and ethyl alcohol at 25°.				
	Ethyl alcohol.	25 p. ct.	50 p. ct.	75 p. ct.	Methyl alcohol.	Ethyl alcohol.	25 p. ct.	50 p. ct.	75 p. ct.	Methyl alcohol.
10	3.53	51.2	7.81	11.44	15.04	4.88	6.39	9.57	13.88	17.98
50	6.42	96.3	14.68	21.10	27.28	8.30	11.83	18.09	25.93	32.98
100	8.48	123.5	18.43	26.08	33.58	12.07	15.48	23.21	32.61	42.37
200	10.20	151.6	22.39	31.28	40.46	13.59	17.47	28.94	39.98	50.06
400	12.01	181.7	26.54	37.33	46.36	17.18	24.18	35.54	48.80	57.78
800	13.95	207.6	29.77	40.95	53.51	19.92	28.58	40.70	53.75	65.78
1600	15.91	239.7	34.83	48.76	60.25	25.24	34.94	48.90	64.12	72.64

Tables 78 and 79 (figs. 82 and 83) show that copper chloride, in mixtures of ethyl alcohol and water, also gives a dropping below the rule of averages for the curves in the 25 per cent and 50 per cent mixtures. Here also, the values between the 75 per cent and 100 per cent mixtures show a general tendency towards the rule of averages. It is to be noted also that there is a bunching of the curves in the 25 per cent and the 50 per cent mixtures, or,

in other words, that there is a comparatively small increase in conductivity with increase in dilution in these mixtures. It is further to be observed that the conductivity values in ethyl alcohol are very much smaller than those in water, although the general increase in conductivity with increase in dilution is about the same in both cases.

The temperature coefficients of conductivity in every case increase with

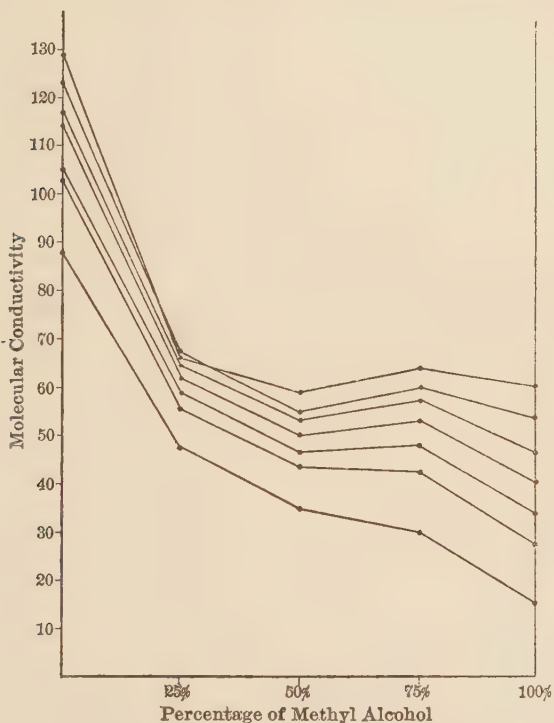


FIG. 80.—CONDUCTIVITY OF COPPER CHLORIDE IN MIXTURES OF METHYL ALCOHOL AND WATER AT 0°.

TABLE 80.—Comparison of the temperature coefficients of conductivity of copper chloride.

ν	In mixtures of methyl alcohol and water from 0° to 25°.					In mixtures of methyl alcohol and ethyl alcohol from 0° to 25°.				
	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.	Ethyl alcohol.	25 p. ct.	50 p. ct.	75 p. ct.	Methyl alcohol.
10	0.0329	0.0421	0.0372	0.0237	0.00984	0.0153	0.00992	0.00901	0.00853	0.00984
50	.0346	.0442	.0403	.0262	.00836	.0117	.00914	.00929	.00916	.00836
100	.0372	.0454	.0414	.0272	.01047	.0169	.01014	.01037	.10002	.01047
200	.0347	.0461	.0416	.0286	.00949	.0133	.00610	.01170	.01113	.00949
400	.0350	.0467	.0431	.0300	.00985	.0172	.01320	.01356	.01229	.00985
800	.0347	.0471	.0435	.0309	.00917	.0171	.01510	.01469	.01250	.00917
1600	.0371	.0475	.0437	.0318	.00823	.0235	.01830	.01616	.01260	.00823

increase in dilution, not with any great regularity, but the values for the most dilute solutions are decidedly greater than those for the most concentrated. Here again, we note that temperature coefficients are larger in the mixtures than they are in either of the pure solvents, and that these values are on the whole largest in the 50 per cent mixture instead of in the 25 per cent, as was the case with methyl alcohol and water.

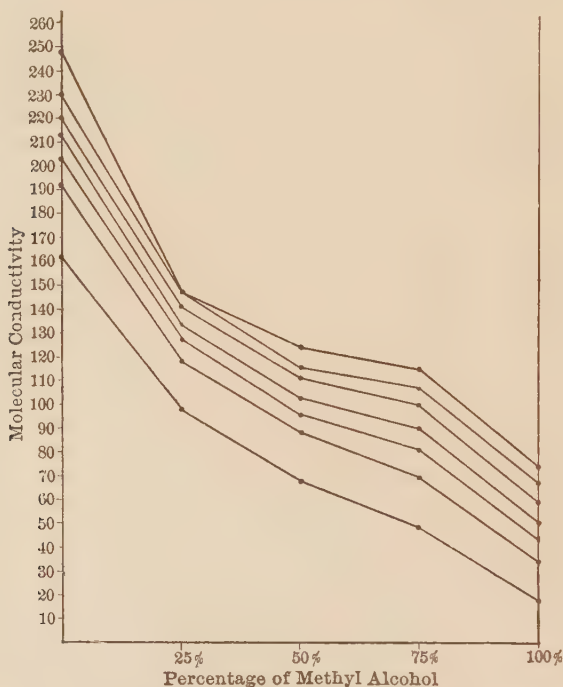


FIG. 81.—CONDUCTIVITY OF COPPER CHLORIDE IN MIXTURES OF METHYL ALCOHOL AND WATER AT 25°.

Tables 78 and 79 (figs. 84 and 85) show that copper chloride, in mixtures of methyl alcohol and ethyl alcohol, gives no minimum in conductivity, but it is to be noted that there is a *decided dropping of the values in the 25 per cent and 50 per cent mixtures*, below the values calculated from the rule of averages, and that this is less pronounced in the more concentrated solutions than in the dilute. A slight exception is found in the case of the N/1600 solution at 25°, where a slight increase in the value above the average value is to be observed in the 75 per cent mixture. The remainder of the curve shows the same decrease in values as is shown by the other curves. Here again it is to be noted that the conductivity values in ethyl alcohol are much smaller than those in methyl alcohol, and increase much less rapidly with the dilution.



FIG. 82.—CONDUCTIVITY OF COPPER CHLORIDE IN MIXTURES OF ETHYL ALCOHOL AND WATER AT 0°.

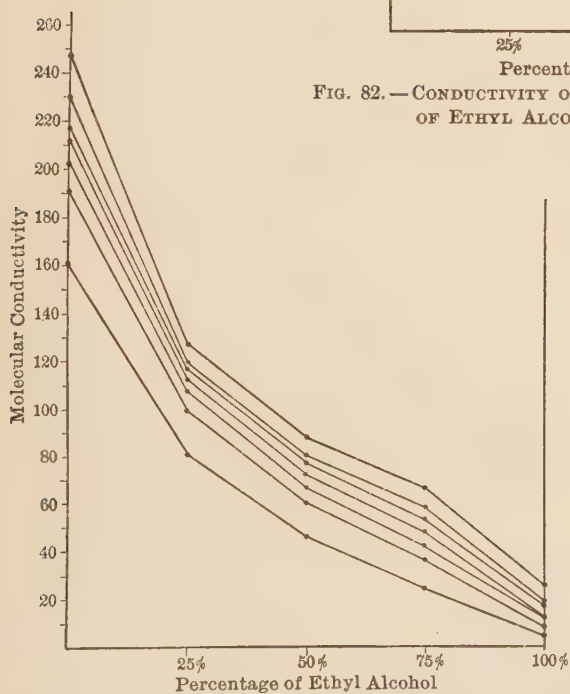


FIG. 83.—CONDUCTIVITY OF COPPER CHLORIDE IN MIXTURES OF ETHYL ALCOHOL AND WATER AT 25°.

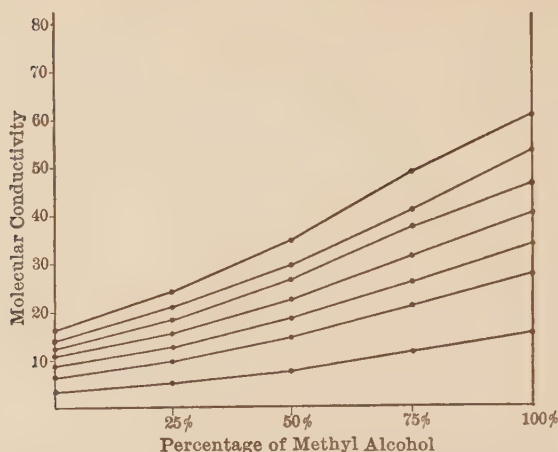


FIG. 84.—CONDUCTIVITY OF COPPER CHLORIDE IN MIXTURES OF METHYL ALCOHOL AND ETHYL ALCOHOL AT 0°.

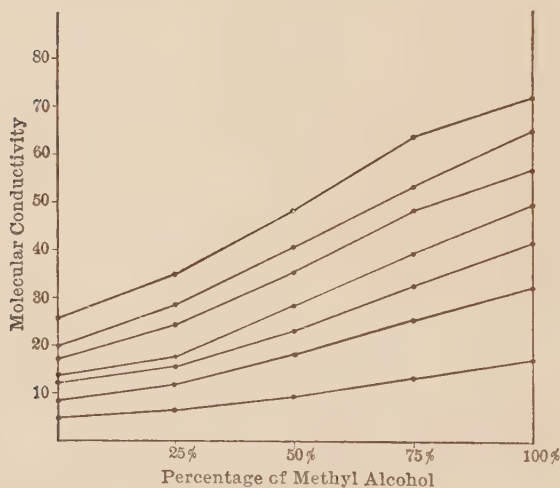


FIG. 85.—CONDUCTIVITY OF COPPER CHLORIDE IN MIXTURES OF METHYL ALCOHOL AND ETHYL ALCOHOL AT 25°.

POTASSIUM SULPHOCYANATE.

The potassium sulphocyanate used in this work was purified in the following manner: The purest salt obtainable was twice recrystallized from redistilled, 95 per cent ethyl alcohol, and then once recrystallized from absolute alcohol. The crystals were drained by suction, and dried at 100°. In every case the salt was crystallized in as finely divided condition as possible. The salt was preserved in glass-stoppered bottles, in a sulphuric acid desiccator.

TABLE 81. — *Conductivity of potassium sulphocyanate at 0° and 25°.*

<i>v</i>	In water.			In a mixture of 25 p. ct. methyl alcohol and water.			In a mixture of 50 p. ct. methyl alcohol and water.		
	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temperature coefficient.	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temperature coefficient.	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temperature coefficient.
10	62.98	112.70	0.0316	37.04	75.00	0.0410	29.59	59.19	0.0400
50	67.42	121.44	.0321	39.09	80.35	.0422	31.35	63.59	.0411
100	68.78	125.06	.0327	39.45	81.14	.0423	31.78	64.62	.0413
200	69.73	126.47	.0326	40.31	82.86	.0422	32.53	66.47	.0417
400	71.62	129.99	.0326	41.19	84.94	.0425	32.63	66.93	.0421
800	71.42	128.96	.0322	41.97	85.29	.0413	32.85	68.17	.0430
1600	72.64	121.61	.0325	41.94	85.84	.0419	33.72	69.87	.0429
<i>v</i>	In a mixture of 75 p. ct. methyl alcohol and water.			In methyl alcohol.			In a mixture of 25 p. ct. ethyl alcohol and water.		
	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temperature coefficient.	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temperature coefficient.	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temperature coefficient.
10	32.06	56.46	0.0304	46.83	64.81	0.0154	27.28	62.60	0.0518
50	35.21	62.77	.0313	56.94	79.40	.0158	28.14	65.90	.0537
100	36.22	64.86	.0316	60.63	84.97	.0161	28.73	67.88	.0545
200	27.34	67.37	.0322	63.78	89.91	.0164	29.51	69.71	.0545
400	37.96	68.75	.0324	66.01	92.91	.0163	29.57	70.73	.0557
800	37.74	70.10	.0343	68.80	97.19	.0165	29.49	71.70	.0573
1600	37.16	69.88	.0352	71.94	102.41	.0169	28.56	71.43	.0600
<i>v</i>	In a mixture of 50 p. ct. ethyl alcohol and water.			In a mixture of 75 p. ct. ethyl alcohol and water.			In ethyl alcohol.		
	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temperature coefficient.	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temperature coefficient.	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temperature coefficient.
10	16.93	41.92	0.0590	15.43	32.73	0.0449	14.72	22.97	0.0224
50	17.39	44.37	.0621	16.66	36.31	.0472	18.97	30.13	.0235
100	17.84	45.79	.0627	17.32	37.89	.0475	20.74	33.15	.0239
200	18.02	46.36	.0629	17.76	39.06	.0480	22.45	36.20	.0245
400	18.23	46.94	.0630	17.95	39.70	.0485	23.66	38.82	.0256
800	18.39	47.13	.0625	18.21	40.34	.0486	24.88	41.02	.0260
1600	18.36	47.56	.0636	18.64	41.38	.0490	25.58	42.73	.0268
<i>v</i>	In a mixture of 25 p. ct. methyl alcohol and ethyl alcohol.			In a mixture of 50 p. ct. methyl alcohol and ethyl alcohol.			In a mixture of 75 p. ct. methyl alcohol and ethyl alcohol.		
	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temperature coefficient.	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temperature coefficient.	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temperature coefficient.
10	21.09	31.85	0.0204	28.60	41.69	0.0183	37.06	52.40	0.0166
50	26.47	40.36	.0210	35.56	52.08	.0186	45.39	64.85	.0172
100	28.89	44.27	.0213	38.55	56.98	.0191	48.95	70.42	.0175
200	30.89	47.66	.0217	40.77	60.30	.0192	51.29	74.17	.0178
400	32.32	50.39	.0222	42.74	64.12	.0200	54.09	78.17	.0178
800	33.37	52.20	.0226	43.94	66.10	.0202	54.95	79.75	.0181
1600	34.98	55.74	.0237	45.40	69.09	.0209	57.55	83.61	.0181
<i>v</i>	In a mixture of 25 p. ct. acetone and water.			In a mixture of 50 p. ct. acetone and water.			In a mixture of 75 p. ct. acetone and water.		
	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temperature coefficient.	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temperature coefficient.	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temperature coefficient.
10	39.47	78.74	0.0398	31.81	63.74	0.0402	34.59	59.07	0.0283
50	40.45	82.36	.0414	33.41	67.59	.0409	38.98	68.02	.0298
100	41.56	84.00	.0409	33.69	68.62	.0415	40.21	70.21	.0298
200	42.82	87.12	.0414	34.70	70.56	.0413	41.93	74.01	.0307
400	43.95	89.18	.0412	35.25	71.68	.0413	43.05	76.00	.0306
800	43.46	87.58	.0406	35.55	72.81	.0419	43.76	77.40	.0308
1600	43.59	87.56	.0404	36.86	76.62	.0432	44.00	78.48	.0312

TABLE 81.—*Conductivity of potassium sulphocyanate at 0° and 25°.*—Continued.

v	In acetone.			In a mixture of 25 p. ct. acetone and methyl alcohol.			In a mixture of 50 p. ct. acetone and methyl alcohol.		
	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temperature coefficient.	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temperature coefficient.	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temperature coefficient.
10	43.44	48.66	0.00481	52.06	69.97	0.0138	53.92	70.51	0.0123
50	69.63	78.84	.00529	63.84	86.48	.0142	67.56	88.93	.0127
100	73.83	87.65	.00749	68.44	93.20	.0145	73.33	97.31	.0131
200	94.45	109.00	.00616	71.95	97.90	.0144	77.99	103.77	.0132
400	105.95	126.81	.00788	75.85	103.58	.0146	82.09	109.93	.0136
800	118.80	141.81	.00775	77.29	106.35	.0150	85.42	114.54	.0136
1600	126.20	151.92	.00815	79.75	101.11	.0157	88.41	119.41	.0140

v	In a mixture of 75 p. ct. acetone and methyl alcohol.			In a mixture of 25 p. ct. acetone and ethyl alcohol.		
	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temperature coefficient.	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temperature coefficient.
10	57.40	71.33	0.00971	23.97	34.28	0.0172
50	74.50	93.21	.01005	30.86	44.55	.0177
100	81.96	104.08	.01080	34.13	49.59	.0181
200	86.53	111.05	.01133	36.43	53.55	.0188
400	94.19	120.98	.01138	38.74	57.54	.0194
800	98.00	126.14	.01148	40.55	60.58	.0198
1600	102.90	133.16	.01176	42.14	63.26	.0201

v	In a mixture of 50 p. ct. acetone and ethyl alcohol.			In a mixture of 75 p. ct. acetone and ethyl alcohol.		
	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temperature coefficient.	$\mu_v 0^\circ$	$\mu_v 25^\circ$	Temperature coefficient.
10	34.62	45.51	0.0126	44.87	546.1	0.00868
50	45.06	60.17	.0134	59.92	744.1	.00967
100	49.92	67.40	.0140	67.52	850.6	.01039
200	53.52	73.13	.0147	72.90	925.1	.01076
400	57.35	79.11	.0152	78.97	1015.6	.01144
800	59.06	82.98	.0162	83.23	1078.6	.01184
1600	60.19	86.54	.0175	87.62	1147.3	.01237

TABLE 82.—*Comparison of the conductivities of potassium sulphocyanate.*

v	In mixtures of methyl alcohol and water at 0°.					In mixtures of methyl alcohol and water at 25°.				
	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.
10	62.98	37.04	29.59	32.06	46.83	112.70	75.00	59.19	56.46	64.81
50	67.42	39.09	31.35	35.21	56.94	121.44	80.35	63.59	62.77	79.40
100	68.78	39.45	31.78	36.22	60.63	125.06	81.14	64.62	64.86	84.97
200	69.73	40.31	32.53	37.34	63.78	126.47	82.86	66.47	67.37	89.91
400	71.62	41.19	32.63	37.96	66.01	129.99	84.94	66.93	68.75	92.91
800	71.42	41.97	32.85	37.74	68.80	128.96	85.29	68.17	70.10	97.19
1600	72.64	41.94	33.72	37.16	71.94	131.61	85.84	69.87	69.88	102.41

v	In mixtures of ethyl alcohol and water at 0°.					In mixtures of ethyl alcohol and water at 25°.				
	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.
10	62.98	27.28	16.93	15.43	14.72	112.70	62.60	41.92	32.73	22.97
50	67.42	28.14	17.39	16.66	18.97	121.44	65.90	44.37	36.31	30.13
100	68.78	28.73	17.84	17.32	20.74	125.06	67.88	45.79	37.89	33.15
200	69.73	29.51	18.02	17.76	22.45	126.47	69.71	46.36	39.06	36.20
400	71.62	29.57	18.23	17.95	23.66	129.99	70.73	46.94	39.70	38.82
800	71.42	29.49	18.39	18.21	24.88	128.96	71.70	47.13	40.34	41.02
1600	72.64	28.56	18.36	18.64	25.58	131.61	71.43	47.56	41.48	42.73

TABLE 82. — *Comparison of the conductivities of potassium sulphocyanate.*—Continued.

<i>v</i>	In mixtures of methyl alcohol and ethyl alcohol at 0°.					In mixtures of methyl alcohol and ethyl alcohol at 25°.				
	Ethyl alcohol.	25 p. ct.	50 p. ct.	75 p. ct.	Methyl alcohol.	Ethyl alcohol.	25 p. ct.	50 p. ct.	75 p. ct.	Methyl alcohol.
10	14.72	21.09	28.60	37.06	46.83	22.97	31.85	41.69	52.40	64.81
50	18.97	26.47	35.56	45.39	56.94	30.13	40.36	52.08	64.85	79.40
100	20.74	28.89	38.55	48.95	60.63	33.15	44.27	56.98	70.42	84.97
200	22.45	30.89	40.77	51.29	63.78	36.20	47.66	60.30	74.17	80.91
400	23.66	32.31	42.74	54.09	66.01	38.82	50.39	64.12	78.17	92.91
800	24.88	33.37	43.94	54.95	68.80	41.02	52.20	66.10	79.75	97.19
1600	25.58	34.98	45.40	57.55	71.94	42.73	55.74	69.09	83.61	102.41

<i>v</i>	In mixtures of acetone and water at 0°.					In mixtures of acetone and water at 25°.				
	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.
10	62.98	39.47	31.81	34.59	43.44	112.70	78.74	63.74	59.07	48.66
50	67.42	40.45	33.41	38.98	69.63	121.44	82.36	67.59	68.02	78.84
100	68.78	41.56	33.69	40.21	73.83	125.06	84.00	68.62	70.21	87.65
200	69.73	42.82	34.70	41.93	94.45	126.47	87.12	70.56	74.10	109.00
400	71.62	43.95	35.25	43.05	105.95	129.99	89.18	71.68	76.00	126.81
800	71.42	43.46	35.55	43.76	118.80	128.96	87.58	72.81	77.40	141.81
1600	72.64	43.59	36.86	44.10	126.20	131.61	87.56	76.62	78.48	151.92

<i>v</i>	In mixtures of acetone and methyl alcohol at 0°.					In mixtures of acetone and methyl alcohol at 25°.				
	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.
10	46.83	52.06	53.92	57.40	43.44	64.81	69.97	70.51	71.33	48.66
50	56.94	63.84	67.56	74.50	69.63	79.40	86.48	88.93	93.21	78.84
100	60.63	68.44	73.33	81.96	73.83	84.97	93.20	97.31	104.08	87.65
200	63.78	71.95	77.99	86.53	94.45	89.91	97.90	103.77	111.05	109.00
400	66.01	75.85	82.09	94.19	105.95	92.99	103.58	109.93	120.98	126.81
800	68.80	77.29	85.42	98.00	118.80	97.19	106.35	114.54	126.14	141.81
1600	71.94	79.75	88.41	102.90	126.20	102.41	111.11	119.41	133.16	151.92

<i>v</i>	In mixtures of acetone and ethyl alcohol at 0°.					In mixtures of acetone and ethyl alcohol at 25°.				
	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.
10	14.72	23.97	34.62	44.87	43.44	22.97	34.28	45.51	54.61	48.66
50	18.97	30.86	45.06	59.92	69.63	30.13	44.55	60.17	74.41	78.84
100	20.74	34.13	49.92	67.52	73.83	33.15	49.59	67.40	85.06	87.65
200	22.45	36.43	53.52	72.90	94.45	36.20	53.55	73.13	92.51	109.00
400	23.66	38.74	57.35	78.97	105.95	38.82	57.54	79.11	101.56	126.81
800	24.88	40.55	59.06	83.23	118.80	41.02	60.58	82.98	107.86	141.81
1600	25.58	42.14	60.19	87.62	126.20	42.73	63.26	86.54	114.73	151.92

TABLE 83. — *Comparison of the temperature coefficients of conductivity of potassium sulphocyanate from 0° to 25°.*

<i>v</i>	In mixtures of methyl alcohol and water.					In mixtures of ethyl alcohol and water.				
	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.
10	0.0316	0.0410	0.0400	0.0304	0.0154	0.0316	0.0518	0.0590	0.0449	0.0224
50	.0321	.0422	.0411	.0313	.0158	.0321	.0537	.0621	.0472	.0235
100	.0327	.0423	.0413	.0316	.0161	.0327	.0545	.0627	.0475	.0239
200	.0326	.0422	.0417	.0322	.0164	.0326	.0545	.0629	.0480	.0245
400	.0326	.0425	.0421	.0324	.0163	.0326	.0557	.0630	.0485	.0256
800	.0322	.0413	.0430	.0343	.0165	.0322	.0573	.0625	.0486	.0260
1600	.0325	.0419	.0429	.0352	.0169	.0325	.0600	.0636	.0490	.0268

TABLE 83.—*Comparison of the temperature coefficients of conductivity of potassium sulphocyanate from 0° to 25°.—Continued.*

ν	In mixtures of methyl alcohol and ethyl alcohol.					In mixtures of acetone and water.				
	Ethyl alcohol.	25 p. ct.	50 p. ct.	75 p. ct.	Methyl alcohol.	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.
10	0.0224	0.0204	0.0183	0.0166	0.0145	0.0316	0.0398	0.0402	0.0283	0.00481
50	.0235	.0210	.0186	.0172	.0158	.0321	.0414	.0409	.0298	.00529
100	.0239	.0213	.0191	.0175	.0161	.0327	.0409	.0415	.0298	.00749
200	.0245	.0217	.0192	.0178	.0164	.0326	.0414	.0413	.0307	.00616
400	.0256	.0222	.0200	.0178	.0163	.0326	.0412	.0413	.0306	.00788
800	.0260	.0226	.0202	.0181	.0165	.0322	.0606	.0419	.0308	.00775
1600	.0268	.0237	.0209	.0181	.0169	.0325	.0404	.0432	.0312	.00815

ν	In mixtures of acetone and methyl alcohol.					In mixtures of acetone and ethyl alcohol.				
	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.
10	0.0154	0.0138	0.0123	0.00971	0.00481	0.0224	0.0172	0.0126	0.00868	0.00481
50	.0158	.0142	.0127	.01005	.00529	.0235	.0177	.0134	.00967	.00529
100	.0161	.0145	.0131	.01080	.00749	.0239	.0181	.0140	.01039	.00749
200	.0164	.0144	.0132	.01133	.00616	.0245	.0188	.0146	.01076	.00616
400	.0163	.0146	.0136	.01138	.00788	.0256	.0194	.0152	.01144	.00788
800	.0165	.0150	.0136	.01148	.00775	.0260	.0198	.0162	.01184	.00775
1600	.0169	.0157	.0140	.01176	.00815	.0268	.0201	.0175	.01237	.00815

Tables 81 and 82 (figs. 86 and 87) show that potassium sulphocyanate gives a decided minimum in conductivity, for all the dilutions studied at 0°, in the 50 per cent mixtures of methyl alcohol and water; and that at 25° the

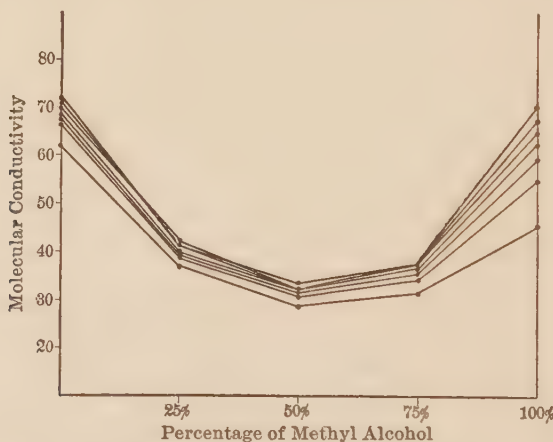


FIG. 86.—CONDUCTIVITY OF POTASSIUM SULPHOCYANATE IN MIXTURES OF METHYL ALCOHOL AND WATER AT 0°.

minimum shifts its position in the first two dilutions to the 75 per cent mixture. It is also to be observed that in the mixtures there is but a very slight increase in molecular conductivity in the more dilute solutions, with increase in dilu-

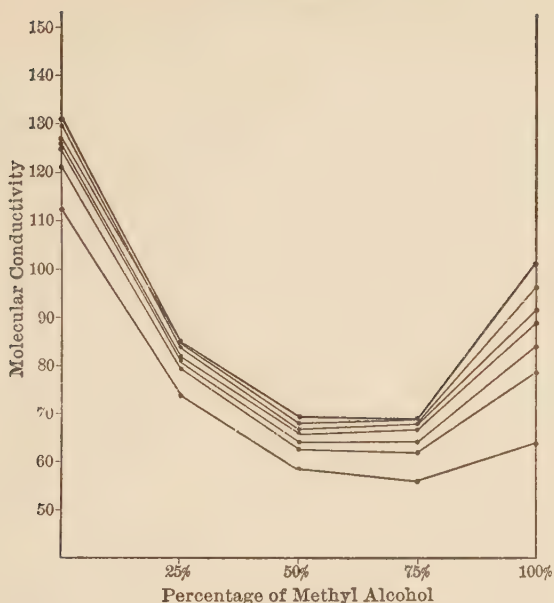


FIG. 87.—CONDUCTIVITY OF POTASSIUM SULPHOCYANATE IN MIXTURES OF METHYL ALCOHOL AND WATER AT 25°.

tion. It is to be noted also that the increase in the conductivity with increase in dilution is greater in methyl alcohol than it is in water, although the values are considerably smaller.

The temperature coefficients of conductivity show in all cases a general increase with increase in dilution, and they are also larger in the 25 per cent and 50 per cent mixtures than in any of the other mixtures of the solvents.

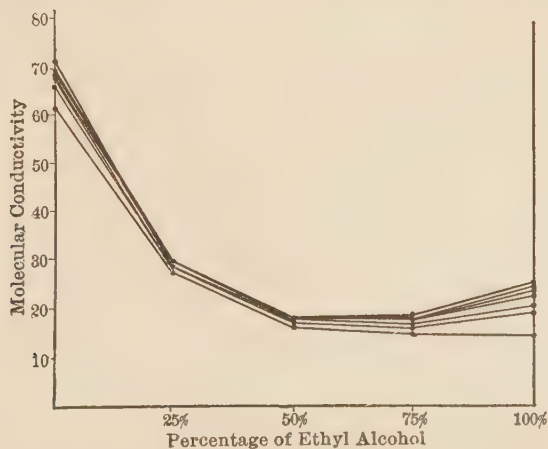


FIG. 88.—CONDUCTIVITY OF POTASSIUM SULPHOCYANATE IN MIXTURES OF ETHYL ALCOHOL AND WATER AT 0°.

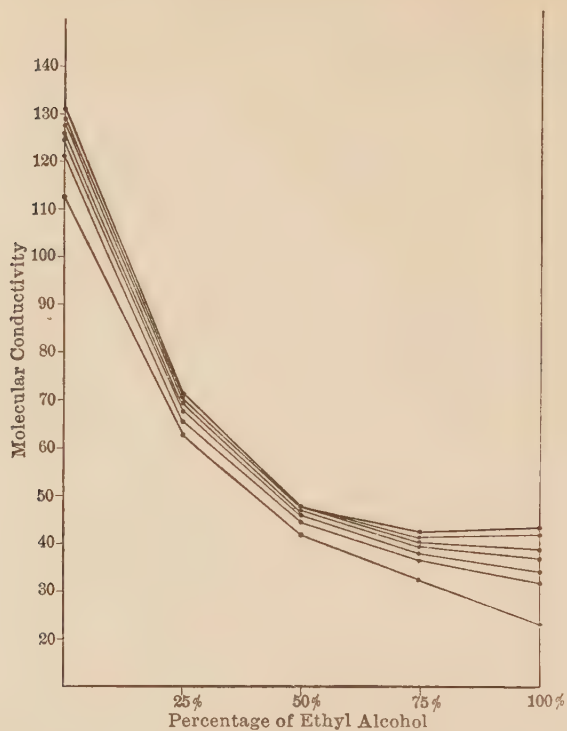


FIG. 89.—CONDUCTIVITY OF POTASSIUM SULPHOCYANATE IN MIXTURES OF ETHYL ALCOHOL AND WATER AT 25°.

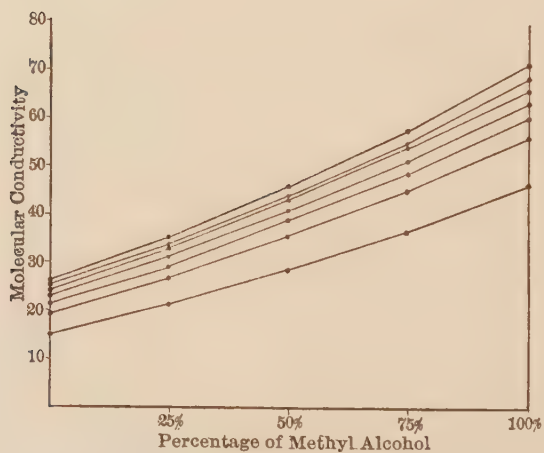


FIG. 90.—CONDUCTIVITY OF POTASSIUM SULPHOCYANATE IN MIXTURES OF METHYL ALCOHOL AND ETHYL ALCOHOL AT 0°.

Tables 81 and 82 (figs. 88 and 89) show that potassium sulphocyanate, in mixtures of ethyl alcohol and water, exhibits a minimum in conductivity at 0° , in the 50 and 75 per cent mixtures, in all cases except the N/10 solution, and at 25° the minimum is shown only in the N/800 and N/1600 solutions, in the 75 per cent mixture. The curves which do not show actual minima, exhibit a decided drop below the average values for the two solvents. They also show that there is only a very slight increase in conductivity with increase in dilution in the mixed solvents, and particularly in the 25 per cent and 50 per cent mixtures. It is to be noted, however, that the increase in conductivity with increase in dilution is greater in ethyl alcohol

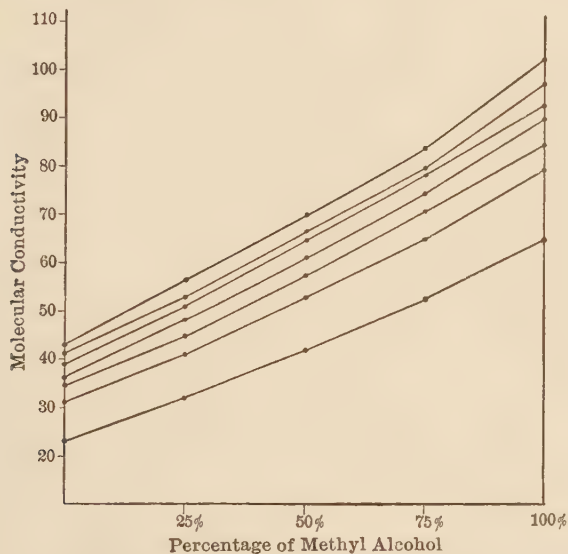
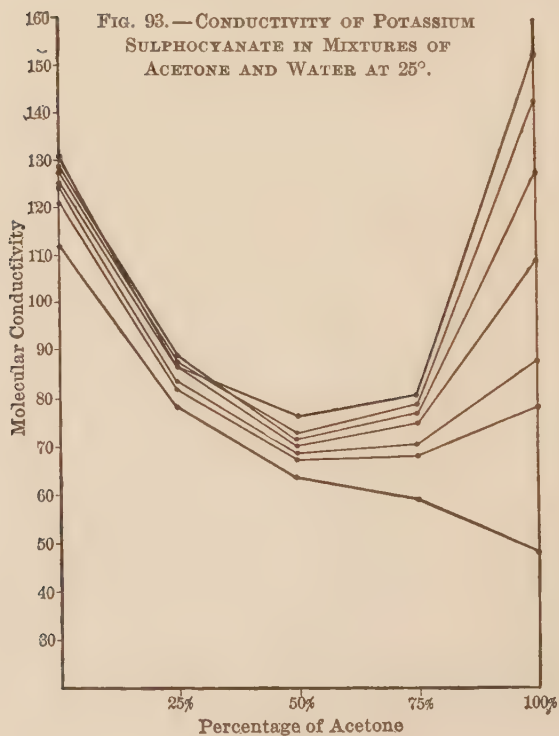
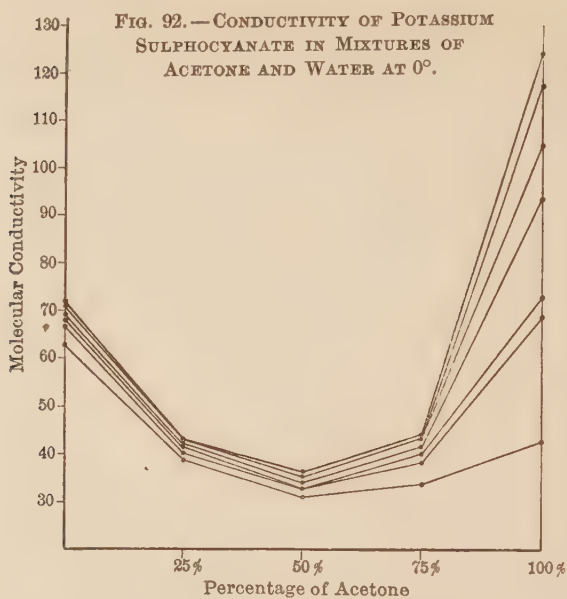


FIG. 91.—CONDUCTIVITY OF POTASSIUM SULPHOCYANATE IN MIXTURES OF METHYL ALCOHOL AND ETHYL ALCOHOL AT 25° .

than it is in water for this particular salt. It is also to be noted that the actual value for conductivity in water is much greater than it is in ethyl alcohol. The temperature coefficients of conductivity show an increase with increase in the dilution of the solution, in every case, and these values are greatest in the 50 per cent mixture.

Tables 81 and 82 (figs. 90 and 91) show that potassium sulphocyanate, in mixtures of methyl alcohol and ethyl alcohol, does not exhibit a minimum in conductivity, but nevertheless there is an appreciable dropping of the curves, plotted from these values, below the average value. It is to be noted also that the increase in conductivity with increase in dilution is practically the average increase as calculated from the increase in the pure solvents. It is



also worthy of note that the conductivity values are greater in methyl alcohol than they are in ethyl alcohol. Here, again, there is a general increase in the value of the temperature coefficients with increase in the dilution of the solution, but in this case the temperature coefficients are greatest in ethyl alcohol and not in the mixtures.

Tables 81 and 82 (figs. 92 and 93) show that potassium sulphocyanate, in mixtures of acetone and water at 0° , exhibits, in all the dilutions studied, a decided minimum in conductivity. It is to be noted, however, that the minimum is somewhat less decided in the most concentrated solution (N/10).

At 25° the minimum occurs in all dilutions except N/10, where it entirely disappears. Here also in the more dilute solutions there is only a slight increase in conductivity, in the mixed solvents, with increase in dilution. It is also seen that even in the case where the minimum in conductivity has disappeared, there is a decided dropping of the curve below the average values. Also the increase in the conductivity in acetone, with increase in dilution, is very much greater than the corresponding increase in water. So great is this difference that although the values are less in acetone for the more concentrated solutions than the corresponding values in water, yet they become much greater in acetone than they do in water for the more dilute solutions.

The temperature coefficients show a general increase with increase in the dilution of the solutions, and the values of the temperature coefficients themselves are greatest in the 50 per cent mixture.

Tables 81 and 82 (figs. 94 and 95) show that potassium sulphocyanate, in mixtures of acetone and methyl alcohol, exhibits a maximum in conductivity in the 75 per cent mixture, for the first three dilutions (N/10, N/50, N/100) at 0° , and for the first four dilutions (N/10, N/50, N/100, N/200) at 25° . Also, that for the more dilute solutions the curves show a decided drop below the average values in the mixtures. It is also to be noted that the increase in conductivity with increase in dilution is very much greater in acetone than it is in methyl alcohol, and, further, that in all the mixtures the increase in conductivity with increase in dilution is practically what would be calculated from the law of averages. Here, again, we note a general increase in the temperature coefficients with increase in dilution, but in this case as in that of potassium sulphocyanate in methyl alcohol and ethyl alcohol, the greatest values do not occur in any of the mixtures, but in one of the pure solvents. In the case of acetone and methyl alcohol the greatest values are in pure methyl alcohol.

Tables 81 and 82 (figs. 96 and 97) show that potassium sulphocyanate, in mixtures of acetone and ethyl alcohol, exhibits a maximum in conductivity in the N/10 solution, in the 75 per cent mixture. However, there is a marked tendency towards a maximum and a very marked increase above the average values in N/50, N/100, and N/200 solutions. The remaining dilutions, while

they do not exhibit a true minimum, do, however, show a dropping below the average values in the mixtures. It is to be observed that the values for conductivity in acetone are much larger than the corresponding values for ethyl alcohol, and also, that the increase in conductivity with increase in dilution is very much larger in acetone than it is in ethyl alcohol. The increase in conductivity with dilution, in the mixtures, is, however, practically what would be calculated from the values in the pure solvents.

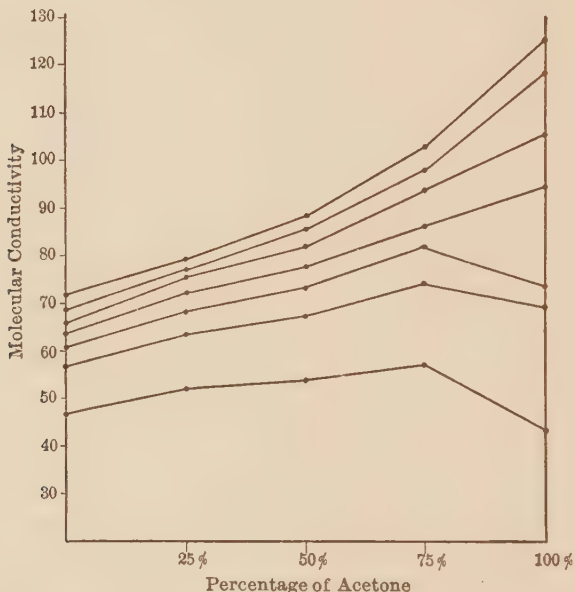
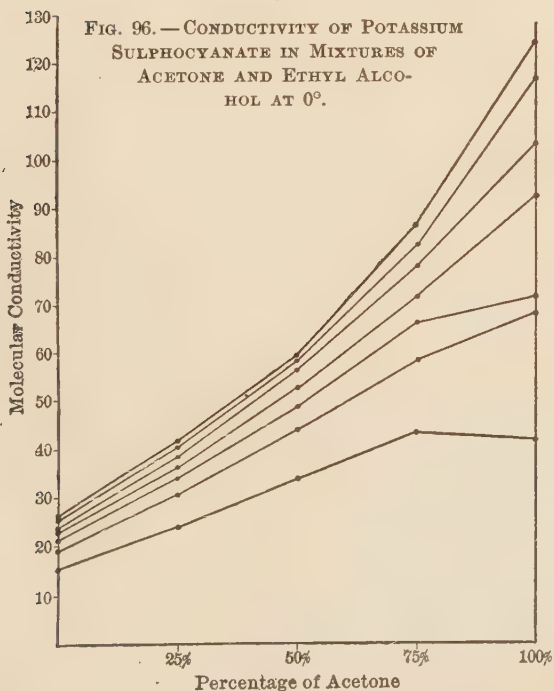
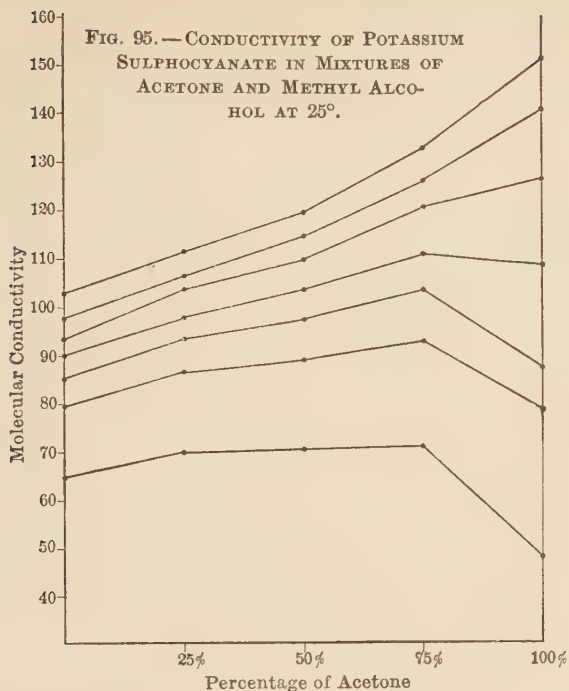


FIG. 94. — CONDUCTIVITY OF POTASSIUM SULPHOCYANATE IN MIXTURES OF ACETONE AND METHYL ALCOHOL AT 0°.

Here, again, as in all the preceding cases, with a very few exceptions, we find a general increase in the temperature coefficients with increase in dilution. In this particular case the coefficients are largest in the pure solvent, ethyl alcohol, and not in the mixtures. A general examination of the temperature coefficients and conductivity in all of the pure solvents and mixtures thus far studied shows that although the increase in conductivity in acetone is relatively very large as compared with the increase in the other solvents, and that the temperature coefficients are relatively very small, yet the percentage increase in the temperature coefficients with increase in dilution is relatively large.



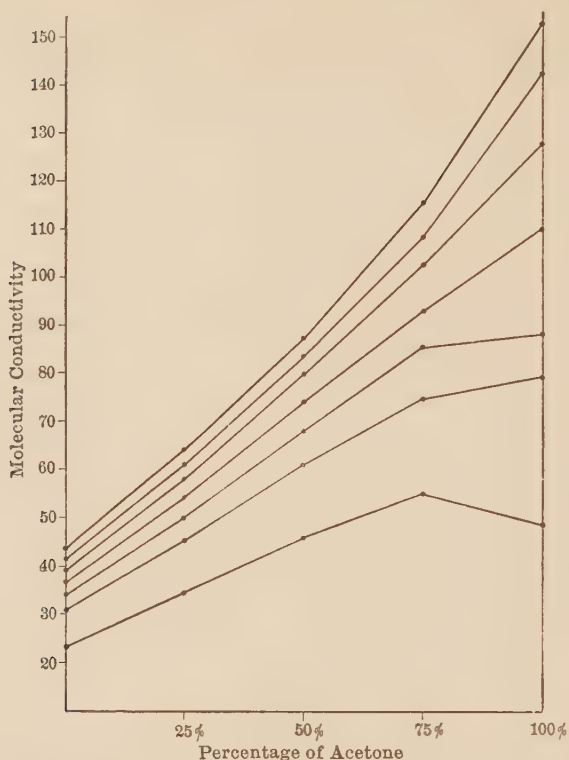


FIG. 97.—CONDUCTIVITY OF POTASSIUM SULPHOCYANATE IN MIXTURES OF ACETONE AND ETHYL ALCOHOL AT 25°.

VISCOSITY MEASUREMENTS.

The method used for measuring the viscosity of solutions throughout this work is that employed by Ostwald.¹ The viscosities have been calculated from the following formula:

$$n = n_0 \frac{St}{S_0 t_0}$$

in which n_0 is the coefficient of viscosity for water, S_0 is the specific gravity of water, and t_0 the time of flow of water through any given capillary at a given temperature; n is the viscosity coefficient of the solution investigated, S is its specific gravity as compared with water as unity at any given temperature, and t is the time of flow of the given solution at that temperature. In the following tables the values for pure water at 0° and 25° were taken from the

¹ Ostwald-Luther: Physiko-chemische Messungen, Aufl. 2, p. 259.

work of Thorpe and Rodger,¹ and these values were used as the basis for the calculation of all the values given in tables 84 to 86.

The fluidity values were calculated from the following formula:

$$\phi = \frac{1}{n}$$

in which ϕ is the fluidity, and n is the corresponding viscosity value. In other words, the fluidity values are simply the reciprocals of the viscosities. All the values given in tables 84 to 86 have been obtained both for pure solvents and solutions, using the modified form of viscometer which has been already described. Many of the values given have been carefully checked by using entirely different solutions in the several determinations.

TABLE 84. — *Fluidity of potassium sulphocyanate at 0° and 25°.*

Mixture.	v	$n0^\circ$	$\phi0^\circ$	$n25^\circ$	$\phi25^\circ$	Temperature coefficient.
In water	10	0.01737	57.58	0.008823	113.34	0.0387
	1600			.008836	113.17	
	Solvent	.01778	56.24	.008910	112.23	.0398
25 p. ct. methyl alcohol and water	10	.03203	31.22	.01297	77.08	.0588
	1600			.01310	76.34	
	Solvent	.03304	30.27	.01312	76.18	.0607
50 p. ct. methyl alcohol and water	10	.03526	28.36	.01462	68.40	.0565
	1600			.01474	67.82	
	Solvent	.03586	27.89	.01477	67.72	.0571
75 p. ct. methyl alcohol and water	10	.02479	40.35	.01201	83.24	.0425
	1600			.01197	83.56	
	Solvent	.02451	40.81	.01196	83.60	.0419
In methyl alcohol	10	.009599	104.18	.006355	157.37	.0204
	1600			.006085	154.34	
	Solvent	.009032	110.72	.006084	165.36	.0194
25 p. ct. ethyl alcohol and water	10	.04904	20.39	.01630	61.35	.0804
	1600			.01653	60.50	
	Solvent	.05135	19.47	.01661	60.19	.0837
50 p. ct. ethyl alcohol and water	10	.06742	14.83	.02148	46.55	.0856
	1600			.02168	46.13	
	Solvent	.07005	14.27	.02170	46.08	.0892
75 p. ct. ethyl alcohol and water	10	.04960	20.16	.01968	50.81	.0608
	1600			.01939	51.57	
	Solvent	.04996	20.01	.01935	51.68	.0633
In ethyl alcohol	10	.02237	44.71	.01261	79.28	.0309
	1600			.01197	83.54	
	Solvent	.02108	47.44	.01145	87.36	.0337

¹ Phil. Trans., 185A, 307 (1894).

TABLE 84.—*Fluidity of potassium sulphocyanate at 0° and 25°.*—Continued.

Mixture.	v	n_0°	ϕ_0°	n_{25}°	ϕ_{25}°	Temperature coefficient.
25 p. ct. acetone and water	10	0.02849	35.10	0.01202	83.20	0.0548
	1600			.01206	82.92	
	Solvent	.02868	34.87	.01205	83.00	.0552
50 p. ct. acetone and water	10	.03006	33.27	.01268	78.88	.0548
	1600			.01260	79.40	
	Solvent	.02992	33.42	.01258	79.52	.0552
75 p. ct. acetone and water	10	.01737	57.58	.009000	111.11	.0372
	1600			.008763	114.12	
	Solvent	.01695	59.00	.008727	114.58	.0377
In acetone	10	.005294	188.91	.004126	242.38	.01132
	1600			.004010	249.36	
	Solvent	.005045	198.24	.003977	251.46	.01074
25 p. ct. acetone and methyl alcohol	10	.007429	134.61	.005380	185.86	.01522
	1600			.005115	195.49	
	Solvent	.006497	153.92	.005087	196.56	.0111
50 p. ct. acetone and methyl alcohol	10	.005632	177.56	.004932	202.74	.00567
	1600			.004675	213.92	
	Solvent	.005177	193.16	.004498	222.33	.00604
75 p. ct. acetone and methyl alcohol	10	.004726	211.62	.004567	218.99	.00139
	1600			.004253	235.12	
	Solvent	.004338	230.54	.004155	240.60	.00175
25 p. ct. methyl alcohol and ethyl alcohol	10	.01707	58.58	.009892	101.10	.0290
	1600			.009500	105.27	
	Solvent	.01617	61.84	.009481	105.48	.0282
50 p. ct. methyl alcohol and ethyl alcohol	10	.01341	74.56	.008270	120.91	.0249
	1600			.007905	126.51	
	Solvent	.01259	79.45	.008009	124.86	.0229
75 p. ct. methyl alcohol and ethyl alcohol	10	.01059	94.46	.007115	140.56	.0195
	1600			.006791	147.24	
	Solvent	.01003	99.68	.006790	147.29	.0191
25 p. ct. acetone and ethyl alcohol	10	.01302	76.80	.007808	128.07	.0267
	1600			.007617	131.29	
	Solvent	.01156	86.53	.007332	136.39	.0231
50 p. ct. acetone and ethyl alcohol	10	.007934	126.04	.006027	165.92	.0127
	1600			.005377	185.98	
	Solvent	.007080	141.24	.005333	187.51	.0131
75 p. ct. acetone and ethyl alcohol	10	.005353	186.81	.004663	214.45	.00592
	1600			.004453	224.57	
	Solvent	.004900	204.07	.004393	227.62	.00462

TABLE 85. — *Comparison of fluidities of potassium sulphocyanate.*

Mixture.	At —	v	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.
Methyl alcohol and water.	0°	10	57.58	31.22	28.36	40.35	104.18
		Solvent	56.24	30.27	27.89	40.81	110.72
	25°	10	113.34	77.08	68.40	83.24	157.37
		1600	113.17	76.34	67.82	83.56	164.34
		Solvent	112.23	76.18	67.72	83.60	164.36
Ethyl alcohol and water	0°	10	57.58	20.39	14.83	20.16	44.71
		Solvent	56.24	19.47	14.27	20.01	47.44
	25°	10	113.04	61.35	46.55	50.81	79.28
		1600	113.17	60.50	46.13	51.57	83.54
		Solvent	112.23	60.19	46.08	51.68	87.36
Acetone and water . .	0°	10	57.58	35.10	33.27	57.58	188.91
		Solvent	56.24	34.87	33.42	59.00	198.24
	25°	10	113.34	83.20	78.88	111.11	242.38
		1600	113.17	82.92	79.40	114.12	249.36
		Solvent	112.23	83.00	79.52	114.58	251.46
Acetone and methyl alcohol	0°	10	104.18	134.61	177.56	211.62	188.91
		Solvent	110.72	153.92	193.16	230.54	198.24
	25°	10	157.37	185.86	202.74	218.99	242.38
		1600	164.34	195.49	213.92	235.12	249.36
		Solvent	164.36	196.56	222.33	240.60	251.46
Acetone and ethyl alcohol	0°	10	44.71	76.80	126.04	186.81	188.91
		Solvent	47.44	86.53	141.24	204.07	198.24
	25°	10	79.28	128.07	165.92	214.45	242.38
		1600	83.54	131.29	185.98	224.57	249.36
		Solvent	87.36	136.39	187.51	227.62	251.46
Methyl alcohol and ethyl alcohol	0°	10	44.71	58.58	74.56	94.46	104.18
		Solvent	47.44	61.84	77.45	99.68	110.72
	25°	10	79.28	101.10	120.91	149.56	157.37
		1600	83.54	105.27	126.51	147.24	164.34
		Solvent	87.36	105.48	124.86	147.29	164.36

TABLE 86. — *Comparison of temperature coefficients of fluidity of potassium sulphocyanate from 0° to 25°.*

Mixture.	v	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.
Methyl alcohol and water . .	10	0.0387	0.0588	0.0565	0.0425	0.0204
	Solvent	.0398	.0607	.0571	.0419	.0194
Ethyl alcohol and water . .	10	.0387	.0804	.0856	.0608	.0309
	Solvent	.0398	.0837	.0892	.0633	.0337
Acetone and water	10	.0387	.0548	.0548	.0372	.0113
	Solvent	.0398	.0552	.0552	.0377	.0107
Acetone and methyl alcohol	10	.0204	.0152	.00567	.00139	.0113
	Solvent	.0194	.0111	.00604	.00175	.0107
Acetone and ethyl alcohol .	10	.0309	.0267	.0127	.00592	.0113
	Solvent	.0337	.0231	.0131	.00462	.0107
Methyl alcohol and ethyl alcohol	10	.0309	.0290	.0249	.0195	.0204
	Solvent	.0337	.0282	.0229	.0191	.0194

Tables 84 and 85 (fig. 98) show that potassium sulphocyanate, in mixtures of methyl alcohol and water, exhibits a marked minimum in fluidity in the 50 per cent mixture at 25° and at 0°, although in the latter case there is only a slight difference between the values in the 25 per cent and the 50 per cent mixtures. *It is of especial importance to note here that potassium sulphocyanate shows a marked negative viscosity (or positive fluidity) in water, and that the viscosity values do not become positive until a mixture about midway between*

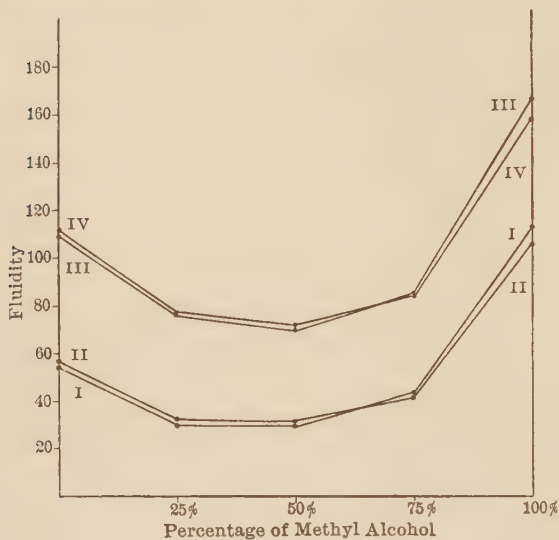


FIG. 98.

Curve I, fluidities of mixture of methyl alcohol and water at 0°.

Curve II, fluidities of N/10 potassium sulphocyanate in mixtures of methyl alcohol and water at 0°.

Curve III, fluidities of the above solvent mixtures at 25°.

Curve IV, fluidities of N/10 potassium sulphocyanate in the above solvent mixtures at 25°.

the 50 per cent and 75 per cent mixtures is reached. In other words, N/10 solution of potassium sulphocyanate in water is much less viscous (or has a much greater fluidity) than pure water itself. On the other hand, a N/20 solution of potassium sulphocyanate in methyl alcohol has a greater viscosity (or smaller fluidity) than the pure solvent itself. These two effects become equal, and we have the viscosity (or fluidity) of the N/10 solution and the pure solvent equal in a mixture intermediate between the 50 per cent and 75 per cent mixtures. The normal or general action of a salt, when dissolved in water, is to increase the viscosity. Cases of negative viscosity have been noted by other workers, and this subject will be discussed later in this memoir. It should be noted that the difference in viscosity between the solution and the pure solvent is greater in methyl alcohol than it is in water, or any of the mixtures. The temperature coefficients of fluidity are greater in the pure solvents than in the solutions, in the 0 per cent, 25 per cent, and 50 per cent mixtures; and *vice versa* in the 75 per cent and 100 per cent mixtures, and

the temperature coefficients of fluidity themselves are greatest in the 25 per cent mixture.

Tables 84, 85, and 86 (fig. 99) show that potassium sulphocyanate, in mixtures of ethyl alcohol and water, exhibits a decided minimum in fluidity in the 50 per cent mixture. Here, also, there is the negative viscosity coefficient in the aqueous mixtures, up to a mixture intermediate between the 50 per cent and 75 per cent mixtures; from this point on it is positive. The difference in viscosity between the solutions and pure solvent is much greater in the pure ethyl alcohol than it is in pure water; and it will also be noted that the difference between the viscosity of the solution and the pure solvent, in the case of ethyl alcohol, is greater at 25° than at 0°. A study of the temperature coefficients of fluidity shows that in all the mixtures they are greater

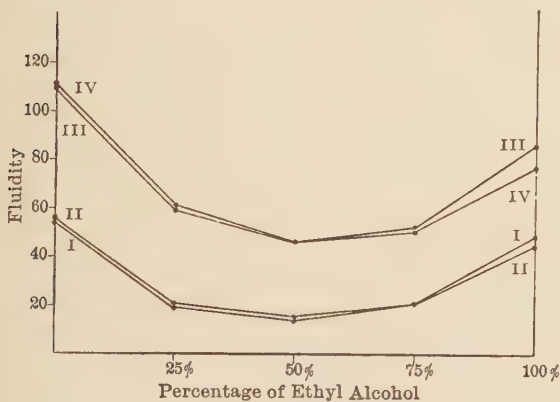


FIG. 99.

Curve I, fluidities of mixtures of ethyl alcohol and water at 0°.

Curve II, fluidities of N/10 potassium sulphocyanate in mixtures of ethyl alcohol and water at 0°.

Curve III, fluidities of the above solvent mixtures at 25°.

Curve IV, fluidities of N/10 potassium sulphocyanate in the above solvent mixtures at 25°.

for the pure solvent than they are for the solution. The temperature coefficients of fluidity are greatest in the 50 per cent mixture.

The temperature coefficients of fluidity decrease with increase in dilution in the 0 per cent, 25 per cent, and 100 per cent mixtures, and increase with increase in dilution in the 50 per cent and 75 per cent mixtures, which are the mixtures in which the maximum fluidity is shown.

Tables 84, 85, and 86 (fig. 100) show that potassium sulphocyanate, in mixtures of acetone and water, exhibits a minimum in the fluidity curves in the 50 per cent mixtures at both 0° and 25°. Here, again, we have the negative viscosity coefficient in the aqueous solutions and in the 25 per cent mixtures. This negative coefficient becomes zero at some point intermediate between the 25 per cent and the 50 per cent mixtures; and is positive from that point on throughout the remaining mixtures. We must also call attention to the fact that the increase in viscosity with increase in dilution is

greater in acetone than it is in water, and that the viscosity of acetone is very much less than that of water.

The temperature coefficients of fluidity increase in all the mixtures, with the exception of the 100 per cent mixtures, with increase in dilution; and the largest coefficients are in the 25 per cent and 50 per cent mixtures; the values in these two cases being identical to the fourth decimal place.

Tables 84, 85, and 86 (fig. 101) show that potassium sulphocyanate, in

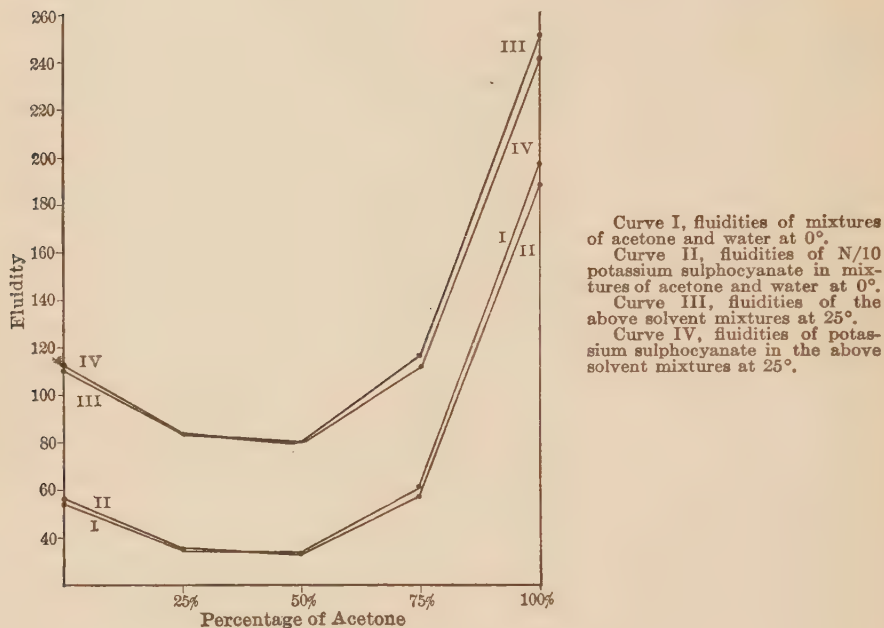


FIG. 100.

mixtures of acetone and methyl alcohol, exhibits a marked maximum which disappeared at 25°. The curves at 25°, however, show an increase in the fluidity at 0°, in the 75 per cent mixtures, but that this maximum has values above the average values for the two solvents. It is to be noted also, that although the increase in fluidity with increase in dilution is nearly the same in acetone and methyl alcohol, yet this increase is very much greater in the mixtures, and especially in the 50 per cent and 75 per cent mixtures.

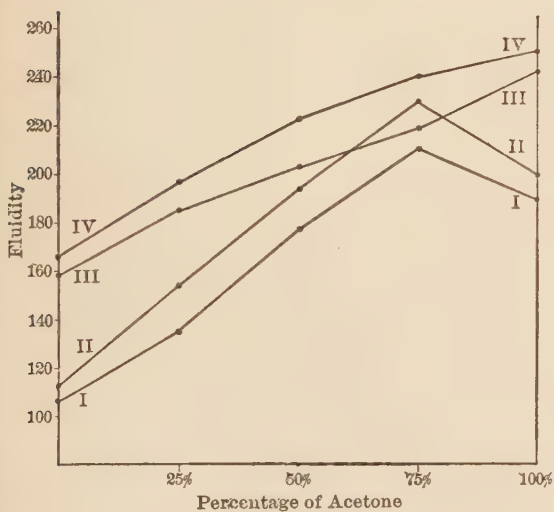
Tables 84, 85, and 86 (fig. 102) show that tenth-normal potassium sulphocyanate, in mixtures of acetone and ethyl alcohol, exhibits a maximum in fluidity in the 75 per cent mixture at 0°. The pure solvent at 0°, and the solutions and solvent at 25°, do not exhibit this maximum, although they do

show an increase above the values calculated on the basis of averages. It is to be noted also that the increase in fluidity with increase in dilution is greatest in the 50 per cent and 75 per cent mixtures.

The temperature coefficients of fluidity increase with increase in dilution in the 0 per cent and 50 per cent mixtures; but decrease with increasing dilution in the 25 per cent, 75 per cent, and 100 per cent mixtures. The largest values are found in the 0 per cent solutions.

Tables 84, 85, and 86 (fig. 103) show that potassium sulphocyanate, in mixtures of methyl alcohol and ethyl alcohol, exhibits an increase in fluidity above the average values in the 50 per cent and 75 per cent mixtures.

The temperature coefficients of fluidity decrease with increase in dilution



Curve I, fluidities of N/10 potassium sulphocyanate in mixtures of acetone and methyl alcohol at 0°.

Curve II, fluidities of mixtures of acetone and methyl alcohol at 0°.

Curve III, fluidities of N/10 potassium sulphocyanate in the above mixtures at 25°.

Curve IV, fluidities of the above solvent mixtures at 25°.

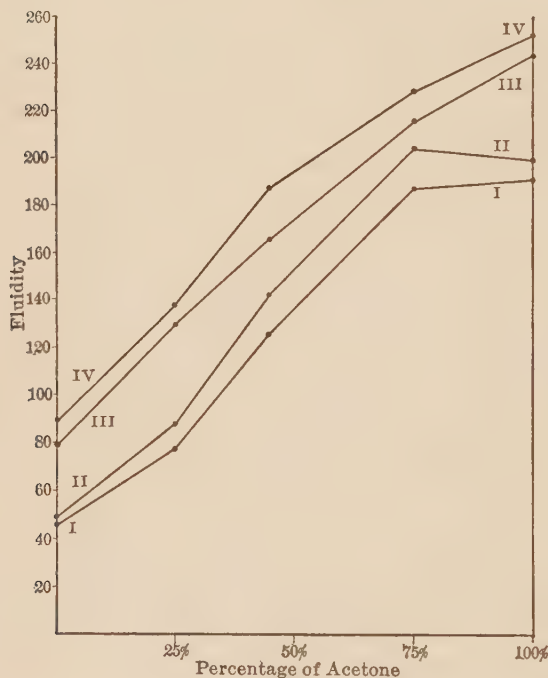
FIG. 101.

in every case, except the 0 per cent mixture, the maximum value being in the 0 per cent mixture.

Table 85 shows that the temperature coefficients of fluidity of potassium sulphocyanate, in mixtures of methyl alcohol and water, increase with increase in dilution of the solutions in the 0 per cent, 25 per cent, and 50 per cent mixtures; and decrease with increase in dilution in the 75 per cent and 100 per cent mixtures. The temperature coefficients of conductivity of copper chloride in these mixtures increase with increasing dilution in every case, except the 100 per cent mixture, where the opposite condition holds. The temperature coefficients of conductivity of potassium sulphocyanate increase with increase in dilution in all of the solvents. The temperature coefficients of fluidity are largest in the 25 per cent mixture, and such is the case also for

the temperature coefficients of conductivity of both copper chloride and potassium sulphocyanate.

Table 87 shows that the temperature coefficients of fluidity of potassium sulphocyanate, in mixtures of ethyl alcohol and water, increase in all cases with increase in dilution. The same is true of the temperature coefficients of conductivity of both copper chloride and potassium sulphocyanate. The temperature coefficients of fluidity are largest in the 50 per cent mixtures,



Curve I, fluidities of N/10 potassium sulphocyanate in mixtures of acetone and ethyl alcohol at 0°.

Curve II, fluidities of mixtures of acetone and ethyl alcohol at 0°.

Curve III, fluidities of N/10 potassium sulphocyanate in the above mixtures at 25°.

Curve IV, fluidities of the above solvent mixtures at 25°.

FIG. 102.

and the same is true of the temperature coefficients of conductivity of both the above-mentioned salts.

Table 87 shows that the temperature coefficients of fluidity of potassium sulphocyanate, in mixtures of acetone and water, increase with increasing dilution, with the exception of the solutions in the pure acetone. The maximum values for these temperature coefficients are found in the 25 per cent and 50 per cent mixtures. The temperature coefficients of conductivity of potassium sulphocyanate, in these mixtures, increase with increase in dilution, the maximum values being in the 50 per cent mixture.

Table 87 shows that the temperature coefficients of fluidity of potassium sulphocyanate, in mixtures of acetone and methyl alcohol, decrease with

increase in dilution in the 0 per cent, 25 per cent, and 100 per cent mixtures, and *vice versa* in the 50 per cent and 75 per cent mixtures. The maximum values are in methyl alcohol. The temperature coefficients of conductivity of potassium sulphocyanate, on the other hand, increase with increase in dilution in every case, and the maximum values are in methyl alcohol.

Table 87 shows that the temperature coefficients of fluidity of potassium sulphocyanate, in mixtures of acetone and ethyl alcohol, increase with increase

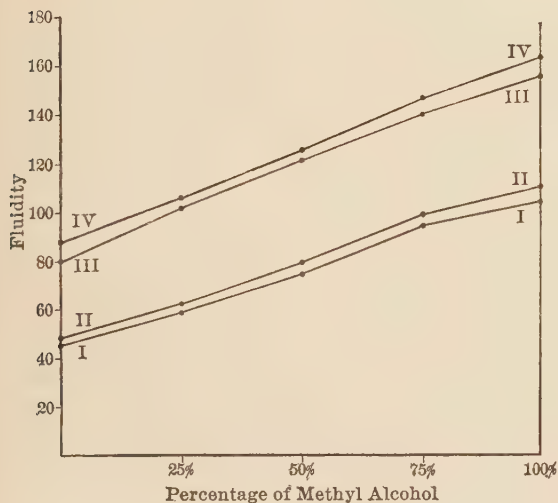


FIG. 103.

Curve I, fluidities of N/10 potassium sulphocyanate in mixtures of methyl alcohol and ethyl alcohol at 0°.

Curve II, fluidities of mixtures of methyl alcohol and ethyl alcohol at 0°.

Curve III, fluidities of N/10 potassium sulphocyanate in the above mixtures at 25°.

Curve IV, fluidities of the above mixed solvents at 25°.

in dilution in the 0 per cent and 50 per cent mixtures, but decrease in the 25 per cent, 75 per cent, and 100 per cent mixtures. The maximum values are in the 0 per cent mixture. The temperature coefficients of conductivity of potassium sulphocyanate in these mixtures increase in every case with increase in dilution. The maximum values are in the 0 per cent mixture.

Table 87 shows that the temperature coefficients of conductivity of copper chloride increase with increase in dilution in all cases, except the 100 per cent mixture, the maximum values being in the 0 per cent mixture.

The corresponding temperature coefficients for potassium sulphocyanate increase with increasing dilution in all cases, and the maximum values are in the 0 per cent mixture.

A SUMMARY OF THE FACTS ESTABLISHED.

(1) A minimum in conductivity has been noted in the following cases: Potassium sulphocyanate in 50 per cent methyl alcohol and water at 0°. This shifts to the 75 per cent mixture at 25°. Also in 50 per cent acetone

and water at 0° and 25°, with the single exception of the N/10 solution at 25°. Likewise, in the 50 per cent and 75 per cent mixtures of ethyl alcohol and water, with the exception of the N/10 solution at 0°. At 25° the N/800 and N/1600 solutions show minimum values, these occurring in the 75 per cent mixture.

TABLE 87. — *Comparison of the temperature coefficients of conductivity and fluidity.*

	<i>v</i>	Dissolved substance.	0 p. ct.	25 p. ct.	50 p. ct.	75 p. ct.	100 p. ct.
In mixtures of methyl alcohol and water.	Fluidity . .	{ 10 KCNS	0.0387	0.0588	0.0565	0.0425	0.0204
		{ Solvent	.0398	.0607	.0571	.0419	.0194
	Conductivity	{ 10 CuCl ₂	.0329	.0421	.0372	.0237	.00984
		{ 1600 CuCl ₂	.0371	.0475	.0437	.0318	.00823
		{ 10 KCNS	.0316	.0410	.0400	.0304	.0154
		{ 1600 KCNS	.0325	.0419	.0429	.0352	.0169
In mixtures of ethyl alcohol and water.	Fluidity . .	{ 10 KCNS	.0387	.0804	.0856	.0608	.0309
		{ Solvent	.0398	.0837	.0892	.0633	.0337
	Conductivity	{ 10 CuCl ₂	.0329	.0543	.0556	.0360	.0153
		{ 1600 CuCl ₂	.0371	.0635	.0683	.0432	.0235
		{ 10 KCNS	.0316	.0518	.0590	.0449	.0224
		{ 1600 KCNS	.0325	.0600	.0636	.0490	.0268
In mixtures of acetone and water.	Fluidity . .	{ 10 KCNS	.0387	.0548	.0548	.0372	.0113
		{ Solvent	.0398	.0552	.0552	.0337	.0107
	Conductivity	{ 10 CuCl ₂	.0329				
		{ 1600 CuCl ₂	.0371				
		{ 10 KCNS	.0316	.0398	.0402	.0283	.00481
		{ 1600 KCNS	.0325	.0404	.0432	.0312	.00815
In mixtures of acetone and methyl alcohol.	Fluidity . .	{ 10 KCNS	.0204	.0152	.00567	.00139	.0113
		{ Solvent	.0194	.0111	.00604	.00175	.0107
	Conductivity	{ 10 CuCl ₂	.00984				
		{ 1600 CuCl ₂	.00823				
		{ 10 KCNS	.0154	.0138	.0123	.00971	.00481
		{ 1600 KCNS	.0169	.0157	.0140	.01176	.00815
In mixtures of acetone and ethyl alcohol.	Fluidity . .	{ 10 KCNS	.0309	.0267	.0127	.00592	.0113
		{ Solvent	.0337	.0231	.0131	.00462	.0107
	Conductivity	{ 10 CuCl ₂	.0153				
		{ 1600 CuCl ₂	.0235				
		{ 10 KCNS	.0224	.0172	.0126	.00868	.00481
		{ 1600 KCNS	.0268	.0201	.0175	.01237	.00815
In mixtures of methyl alcohol and ethyl alcohol.	Fluidity . .	{ 10 KCNS	.0309	.0290	.0249	.0195	.0204
		{ Solvent	.0337	.0282	.0229	.0191	.0194
	Conductivity	{ 10 CuCl ₂	.0153	.00992	.00901	.00853	.00984
		{ 1600 CuCl ₂	.0235	.01831	.01620	.01260	.00823
		{ 10 KCNS	.0224	.0204	.0183	.0166	.0154
		{ 1600 KCNS	.0268	.0237	.0209	.0181	.0169

(2) A decided fall below the average values for the two pure solvents has been noted in the following mixtures: (a) Copper chloride in methyl alcohol and water, the fall being most pronounced in the 50 per cent mixture; in ethyl alcohol and water in the 25 per cent and 50 per cent mixtures; in methyl alcohol and ethyl alcohol in the 25 and 50 per cent mixtures. (b) Potassium sulphocyanate in mixtures of methyl alcohol and ethyl alcohol, the concentrations being N/400, N/800, and N/1600; in mixtures of acetone and methyl alcohol, and in the mixtures of acetone and ethyl alcohol.

(3) It has been noted that in every case where there is not an actual minimum shown by the curves, but simply the falling below the average values, there is a wide difference between the conductivity values in the two unmixed or pure solvents. It is quite evident that this difference must play a large

part in determining whether there will be an actual minimum in the curves or not; and we wish especially to point out the fact that although an actual minimum is not shown in every case, yet we have virtually a minimum in the conductivity values whenever the pure solvents are mixed; and that this minimum occurs in the 50 per cent and 75 per cent mixtures. There are only a very few exceptions to the above statement, and these exceptions will be pointed out in paragraph 4.

(4) A maximum in conductivity has been noted in the following cases: Potassium sulphocyanate in 75 per cent acetone and methyl alcohol in the N/10, N/50, and N/100 solutions at 0°, and in the N/10, N/50, N/100, and N/200 solutions at 25°. In acetone and ethyl alcohol the N/10 solutions, in the 75 per cent mixture, show a pronounced maximum; and a decided tendency towards a maximum is shown by the N/50, N/100, and N/200 solutions.

(5) It has been noted that there is a marked difference not only between the actual numerical values for molecular conductivity, but also between the corresponding increase in the values with increase in dilution, for copper chloride (a ternary electrolyte) and potassium sulphocyanate (a binary electrolyte) in a given pure solvent. In pure water, for example, the conductivity of copper chloride at 25° increases from 162.6, in the N/10 solution, to 249.7, in the N/1600 solution, while the conductivity of potassium sulphocyanate under the same conditions increases from 112.7 to 131.6.

In other words, the conductivity values for copper chloride in water are much greater than the corresponding values for potassium sulphocyanate.

In pure methyl alcohol the conductivity of copper chloride at 25° increases from 17.98 to 72.64, while the conductivity of potassium sulphocyanate under the same conditions increases from 64.81 to 102.41. Thus we see that although the conductivity of copper chloride, in water, is much greater than the conductivity of potassium sulphocyanate in aqueous solution, yet in methyl alcohol exactly the reverse is true, *i. e.*, the conductivity of copper chloride in methyl alcohol is much less than that of potassium sulphocyanate under the same conditions.

In pure ethyl alcohol the conductivity of copper chloride at 25° increases from 4.88 to 25.24. Potassium sulphocyanate, on the other hand, under the same conditions, increases from 22.97 to 42.73.

Data similar to those just referred to have been obtained by other workers in this field. From the work of Jones and McMaster¹ we see that lithium bromide (a binary electrolyte) shows an increase in conductivity from the N/10 solution to the N/1600 solution in water, of from 86.09 to 106.23.

Cobalt chloride (a ternary electrolyte) shows an increase of from 156.36 to 221.50, over the same range in dilution.

¹ Amer. Chem. Journ., **36**, 335-381 (1906).

In methyl alcohol they found that lithium bromide increases from 50.21 to 83.64, and cobalt chloride from 41.78 to 133.33 for the same increase in dilution.

In ethyl alcohol lithium bromide increases from 17.22 to 33.36; and cobalt chloride from 7.64 to 33.59, between the N/10 and the N/1600 solutions.

In acetone lithium bromide increases from 110.82 to 85.90 over the above range in dilution, and cobalt chloride increases from 9.47 in the N/100 solution to 10.45 in the N/1600 solution.

Jones and Bingham¹ obtained the following data with lithium nitrate, potassium iodide, and calcium nitrate: Lithium nitrate in water, between the N/10 and N/1600 solutions increases from 83.9 to 102.8; potassium iodide in water between the N/200 and N/1600 solutions increases from 136.3 to 140.7; calcium nitrate in water between the N/10 and N/1600 solutions increases from 165.5 to 249.8. Here, again, we observe that the ternary electrolytes show a much greater conductivity in aqueous solutions than do the binary electrolytes.

Lithium nitrate in methyl alcohol, between the N/10 and N/1600 solutions increases from 51.31 to 86.7; potassium iodide in methyl alcohol between the N/200 and N/1600 solutions increases from 91.4 to 103.3; calcium nitrate in methyl alcohol between the N/10 and the N/1600 solutions increases from 17.17 to 35.4; potassium iodide in ethyl alcohol between the N/200 and N/1600 solutions increases from 34.6 to 42.8.

Calcium nitrate in ethyl alcohol between the N/10 and the N/1600 solutions increases from 7.86 to 33.3; lithium nitrate in acetone under the same conditions increases from 10.87 to 59.8; potassium iodide in acetone between the N/200 and the N/1600 solutions increases from 118.0 to 141.1; and calcium nitrate in acetone between the N/10 and the N/1600 solutions increases from 5.67 to 12.62.

(6) The temperature coefficients of conductivity increase with increase in dilution, with one exception. This exception is copper chloride in methyl alcohol. The increase is not regular, but it is quite decided when the difference in the values for the N/10 and the N/1600 solutions is considered.

(7) The temperature coefficients of conductivity are always a maximum in the mixtures of water with the alcohols or acetone, and are never a maximum in the mixtures of the alcohols with each other or with acetone.

The individual facts upon which the above statement is based are as follows: Copper chloride in 25 per cent methyl alcohol and water; in 50 per cent ethyl alcohol and water; potassium sulphocyanate in 25 per cent and 50 per cent mixtures of methyl alcohol and water, and in 50 per cent acetone and water, and in 50 per cent ethyl alcohol and water.

The data obtained by Jones and McMaster² show that this is also true for

¹ Amer. Chem. Journ., **34**, 497-534 (1905).

² Loc. cit.

lithium bromide in 25 per cent methyl alcohol and water, in 50 per cent ethyl alcohol and water, and in 50 per cent acetone and water. It is also true for cobalt chloride, in 25 per cent methyl alcohol and water, in 50 per cent ethyl alcohol and water, and in 75 per cent acetone and water.

By reference to the work of Jones and Bingham ¹ we see that this is likewise true for lithium nitrate in 25 per cent acetone and water, for potassium iodide in 50 per cent acetone and water, and for calcium nitrate in 25 per cent and 50 per cent acetone and water.

(8) The molecular conductivities of potassium sulphocyanate in acetone, as compared with the corresponding conductivities in water, bring out some important facts. The conductivity values in the N/10 solutions are usually much smaller in acetone than they are in water, but with increase in dilution they become very much larger in acetone than they do in water. The same thing is seen to be true when the conductivity of the acetone solutions is compared with the solutions in the alcohols, but to a smaller degree. The values become greater in acetone than they do in either of the alcohols.

(9) A marked minimum in fluidity has been noted in the following cases: 50 per cent methyl alcohol and water at 0° and 25°, 50 per cent ethyl alcohol and water, 50 per cent acetone and water.

(10) A maximum in fluidity has been noted in the following cases: In 75 per cent acetone and methyl alcohol at 0°. Although this maximum has disappeared at 25°, yet there is a decided increase of the values in the mixture above the average values; in N/10 potassium sulphocyanate in 75 per cent acetone and ethyl alcohol at 0°. The pure solvent does not show the maximum at 0°, and the maximum has entirely disappeared at 25° in both the solution and the solvent, but nevertheless there is an increase above the average values in each case in the 75 per cent mixture. This increase above the average values is also shown by the mixtures of methyl alcohol and ethyl alcohol.

(11) A marked negative viscosity coefficient is shown by potassium sulphocyanate in aqueous solution. In the other pure solvents, methyl alcohol, ethyl alcohol, and acetone, potassium sulphocyanate gives a positive viscosity coefficient, and in mixtures of the other solvents with water the viscosity coefficient becomes zero in the following mixtures: At a point about midway between the 50 per cent and 75 per cent mixtures of methyl alcohol and water; and in the same mixtures of ethyl alcohol and water, and between the 25 per cent and 50 per cent mixtures of acetone and water.

(12) The temperature coefficients of fluidity are a maximum in the mixtures of the other solvents with water in the 25 and 50 per cent mixtures, and in no case are they a maximum in the mixtures of the alcohols and acetone with one another.

¹ Loc. cit.

DISCUSSION OF RESULTS.

It would be desirable for some reasons to discuss the facts brought out by our study of conductivity in one section, and the results of the work on fluidity in a separate section; but on account of the close relations between conductivity and fluidity it seems best to take up the discussion in such a manner as to bring out more clearly the bearing of these relations upon one another.

An explanation of the minimum in molecular conductivity has been offered by Jones and Lindsay,¹ and, as has already been pointed out in the introductory section of this paper, this has been experimentally substantiated by the work of Jones and Murray.¹ This explanation was, however, applied only to the cases where an actual minimum occurs, but, as we have already pointed out, there are fully as many cases in which the curves show simply a falling below the values as calculated from the rule of averages. We have shown that in these cases we have what we may call a *virtual minimum*, and we extend the hypothesis of Jones and Lindsay to these cases also, since it bears as we believe on both the actual minima and the virtual minima. Since these two conditions cover by far the greater majority of the conductivity results that have been obtained up to the present in mixed solvents, it appears that the hypothesis of Jones and Lindsay when applied to the problem of conductivity in mixed solvents is perfectly general.

A further proof of this explanation has been brought out by our study of fluidity. A marked minimum in fluidity occurs in the 50 per cent mixtures of water and methyl alcohol, water and ethyl alcohol, and water and acetone. It is in these same mixtures that the minimum in conductivity occurs.

F. H. Getman,² in discussing the maximum viscosity (or minimum fluidity, which occurs when the alcohols and water are mixed, drew the conclusion that if the association of one liquid is diminished by the presence of another associated liquid, then the viscosity of a 50 per cent mixture of these liquids should be less than the viscosity as calculated from the rule of averages. This conclusion, as we shall see, is erroneous. The work of Thorpe and Rodger³ has clearly shown that viscosity may be taken as the sum of the forces in play between the molecules. Therefore, when two associated liquids are mixed, if they mutually decrease the association of one another, the total number of molecules in a given volume of the mixtures is increased, and consequently

¹ Loc. cit.

² Journ. chim. Phys., **4**, 403 (1906).

³ Phil. Trans., **185A**, 307 (1894).

the total surface of the molecules of the solvents is increased, *i. e.*, the *total frictional surface is increased*, and an *increase in viscosity results*. The point at which the viscosity of the mixed solvents becomes a maximum, is, then, the point at which the effect above mentioned of the pure solvents on each other is the greatest. Thus we see that at the point where we find the maximum in viscosity we have the greatest number of simple molecules of the two solvents present.

According to this view of the cause of the fluidity minimum (or viscosity maximum), the reason for the minimum in the conductivity curve follows at once. Since the association of the solvents is a minimum at the point of minimum fluidity, the dissociating power of the solvents is also at a minimum, and the minimum in conductivity is a natural consequence.

As has already been stated, it is at the minimum points of conductivity that we have the phenomenon of a very small increase in molecular conductivity with increase in dilution, as is shown by the conductivity curves for the different dilutions approaching one another as they approach the minimum. This also is a natural consequence of our theory. The association of the solvents being a minimum at these points, as has already been shown, their dissociating power is also a minimum, and, consequently, an increase in the amount of the solvent present has little influence on the dissociation of the dissolved salt. To elaborate this a little more fully, let us suppose that the salt were dissolved in a solvent which had no dissociating power; then no matter how much of the solvent were present, the dissociation of the salt and, consequently, the molecular conductivity of the solution, would remain zero. If, now, a solvent is used which has very small dissociating power, it is evident that comparatively large amounts of it would be required to produce any very appreciable effect upon the dissociation of the dissolved salt.

In a few cases a maximum in conductivity was observed. These cases occur in certain of the mixtures of acetone with the alcohols. Similar examples, and in these same solvents, were first observed by Jones and Bingham,¹ who suggested the explanation that these maxima are due either to an increase in the number of ions present, or to a diminution in the size of the ionic spheres, making possible a more rapid movement of the ions. As has been pointed out, their final conclusion is that the latter explanation, *i. e.*, a diminution in the size of the ionic spheres, is the more probable. The question, however, arises: Why does this change in the size of the ionic spheres take place?

The experimental data, obtained up to the present, are not sufficient to justify a final answer to this question. We offer the following suggestion, however, as probable: The *increase in fluidity*, in view of what has already been said with regard to the cause of maxima and minima in the fluidity

¹ Loc. cit.

curves, is *probably due to an increase in the molecular aggregation of the solvent*. This increase is not necessarily caused by an increase in the association of either of the pure solvents. Indeed, the association of the pure solvents is in all probability less in the mixtures. The increase in molecular aggregation above referred to may simply be due to a molecular combination of the unassociated parts of the pure solvents. The view that is now generally held with regard to chemical combination is that such combination usually takes place between the ions and not between the molecules. We may, in a sense, regard a molecule that is broken down into its ions as in a state of diminished atomic aggregation, just as we regard the diminution in association, when two pure solvents are mixed, as a state of diminished molecular aggregation. The ions, to be sure, are in a different physical condition from the undissociated molecule, in that they carry equal and opposite electrical charges; and we have no experimental reason whatsoever for supposing that the unassociated portions of the solvent molecules, in the mixed solvents, are in the same condition. It is, however, the difference in energy relations between the ions that is at the basis of our present views of chemical combination. Reasoning from analogy, it is not unthinkable, to say the least, that a similar although not identical difference in energy relations is the cause of molecular aggregation or association. If such an energy relation as has been referred to does exist, then we have an explanation of the formation of complex molecules, such as hydrates, double salts, etc. If the above reasoning is correct, the explanation of the fluidity maximum is simple. According to Ramsay and Shields¹ the molecular complexity of the four solvents is as follows:

Substance.	Molecular complexity between 0° and 25°.
Water	(H ₂ O) ₄ .
Methyl alcohol	(CH ₃ OH) _{3.4}
Ethyl alcohol	(C ₂ H ₅ OH) _{2.7}
Acetone	(CH ₃ COCH ₃) _{1.26}

From these data we see that the molecules of methyl alcohol and the molecules of ethyl alcohol are much more complex than the molecules of acetone. For the sake of simplicity we shall limit our discussion to the case of mixtures of acetone and methyl alcohol. The maximum in fluidity occurs in the 75 per cent mixture of the two solvents. We should expect the effect of the acetone upon the methyl alcohol to be greatest in about this mixture, because of the relatively large mass of the acetone present; and, consequently, in such a mixture we should have the largest number of unassociated molecules of methyl alcohol. This is shown to be the case by reference to the temperature

¹ Ztschr. phys. Chem., 12, 433 (1893).

coefficients of fluidity of the pure solvents, which are a minimum in the 75 per cent mixture. The methyl alcohol, being much more associated than the pure acetone, a small mass of it would cause a proportionally greater decrease in the association of the acetone, and in about the 75 per cent mixture we should expect to find the condition for molecular combination of these two solvents most favorable. The complex molecule thus formed explains the fluidity maximum, in terms of the view of viscosity and fluidity maxima and minima that we have already suggested. Since the fluidity of the solvent has become much greater, the ionic velocity is increased.

Thus we conclude that the maximum in conductivity is dependent upon two factors: *The change in the size of ionic spheres and the change in the fluidity of the solvent.*

Reference to the work of J. J. Thompson,¹ Brühl,² Nernst,³ Ciamician,⁴ Dutoit and Aston,⁵ Ramsay and Shields,⁶ Crompton,⁷ and Donnan⁸ shows that the prevailing idea concerning the action of dissociating solvents upon dissolved electrolytes is that the dissociating action of the solvent is mainly a function of the dielectric constant and the degree of association of the solvent. We wish, however, to call attention again to the fact that the dissociating action of the solvent is also dependent largely upon the nature of the dissolved electrolyte. We have already seen that the conductivity of copper chloride in water is much greater than the corresponding conductivity of potassium sulphocyanate in water. Now if the dissociating action of all solvents were solely a function of the properties of the solvent, we should expect the conductivity of copper chloride in any other solvent to be greater than the corresponding conductivity of potassium sulphocyanate in that solvent. But such is not the case, since we find that in methyl alcohol, for example, the conditions are exactly the reverse of what they are in water, and, further, that potassium sulphocyanate has a much greater conductivity in methyl alcohol than copper chloride has under the same conditions.

A number of other similar cases have been mentioned in the "General summary of facts established" in this section. These facts show conclusively that the nature of the dissolved salt also plays a large part in determining what the dissociating action of any given solvent will be. The probable explanation of the marked difference in the action of dissociating solvents towards binary and ternary electrolytes is, in the case of water and methyl alcohol for example, as follows: Water, being a highly associated solvent, has the power of breaking down the ternary electrolytes into the simplest ions, each molecule of the ternary electrolyte yielding three ions.

¹ Phil. Mag., **36**, 320 (1893).

² Ztschr. phys. Chem., **13**, 531 (1894).

³ Ibid., **18**, 514 (1895); **27**, 319 (1898); **30**, 1 (1899).

⁴ Ibid., **6**, 403 (1890).

⁵ Compt. rend., **125**, 240 (1897).

⁶ Ztschr. phys. Chem., **12**, 433 (1893).

⁷ Journ. Chem. Soc., **71**, 925.

⁸ Phil. Mag., (6) **15**, 305.

Methyl alcohol, on the other hand, being less associated than water, probably has the power to break down the ternary electrolytes into only two ions, whereas the binary electrolytes are broken down into ions in both the water and the alcohol. The increase in the temperature coefficients with increase in dilution in aqueous solutions has been explained by Jones,¹ and the same explanation doubtless holds for the increase in the temperature coefficients with increase in dilution in the mixed solvents. In the mixed solvents we probably have a sphere around the ions, which is composed of molecules of both the pure solvents. The fact that such solvates are formed in other solvents than water has been established by the work of Jones and McMaster.²

The temperature coefficients of conductivity are a maximum in the 25 per cent and 50 per cent mixtures of water and the other solvents, as has already been pointed out. At first glance this seems to be a remarkable fact, in view of the large amount of experimental evidence that has been furnished by Jones and his co-workers upon the hydrate theory as proposed by Jones. There seems to be but one explanation, viz, that in these particular mixtures the most complex solvates are formed. These complex solvates change in complexity more rapidly with change in temperature than the less complex solvates, and, consequently, the temperature coefficients are a maximum. The question, however, naturally arises, Why are the solvates more complex in one mixture than in another? It will be observed that the maximum temperature coefficients of conductivity in mixtures of methyl alcohol and water are found, as a rule, in the 25 per cent mixtures; yet they also occur in some cases in the 50 per cent mixtures. The maximum values of these temperature coefficients of conductivity in mixtures of ethyl alcohol and water occur most frequently in the 50 per cent mixture, although in some cases they are found in the 25 per cent mixture.

The maximum values of the temperature coefficients of conductivity in mixtures of acetone and water are mainly in the 50 per cent mixture, a few values occurring in the 75 per cent mixture. These facts are significant when considered in the light of the degree of association of the solvents involved, as shown by the table previously given.

Acetone being the least associated of this group of solvents, we should expect its greatest action in diminishing the association of water to occur in about the 75 per cent mixture, where the mass of the acetone is very great. We should expect this effect to manifest itself in the smaller percentage mixtures, when mixtures with water, of more highly associated solvents than acetone, are considered. A glance at the fluidity values shows that although mixtures of methyl alcohol and water show a minimum in the 50 per cent

¹ Amer. Chem. Journ., **35**, 445 (1906).

² Ibid., **35**, 316 (1906).

mixture, yet there is a much more pronounced tendency towards a minimum in the 25 per cent mixture than there is in the 75 per cent mixture. We see also that although the mixtures of ethyl alcohol and water show a minimum in the 50 per cent mixture, yet there is a more marked tendency towards a minimum in the 75 per cent mixture than there is in the 25 per cent mixture. The case of mixtures of acetone and water is not quite so clean cut, but here again the minimum in fluidity is in the 50 per cent mixture; and although the actual value of the fluidity in the 75 per cent mixture is greater than it is in the 25 per cent mixture, yet, when the very great difference between the fluidity of acetone and the fluidity of water is considered, it is readily seen that in this case also the tendency towards a minimum in fluidity is more marked in the 75 per cent mixture than it is in the 25 per cent mixture.

These facts show clearly that in about the 25 and 50 per cent mixtures of the other solvents with water we have the most favorable conditions for the formation of molecular aggregations, such as solvates, between the ions of the dissolved salt and the molecules of the solvents. In other words, we should have the greatest number of simple solvent molecules present in the mixtures above mentioned; and, as we have already pointed out in another connection, these are the conditions under which we can most reasonably expect the greatest combination between the solvent and the dissolved salt.

The fact that the molecular conductivities of potassium sulphocyanate in acetone are smaller than they are in water for the more concentrated solutions, but are much greater in acetone than they are in water for the more dilute solutions, might be due to several causes.

First, a much greater degree of dissociation, and a more rapid increase in dissociation with increase in dilution, in acetone than in water. This view, however, is untenable in view of the fact that acetone is very much less associated than water, and has a much smaller dielectric constant. Indeed, these facts lead us to the conclusion that potassium sulphocyanate is much less dissociated in acetone than it is in water.

Second, a much greater velocity of the ions in acetone than in water. That this is the probable explanation is shown by the following considerations: The fluidity of acetone is very much greater than the fluidity of water, and this, to be sure, is one of the factors that governs an increase in the ionic velocity; but a far more important factor becomes manifest from a study of the temperature coefficients of conductivity. It is a very significant fact that the temperature coefficients of conductivity in water are nearly ten times as great as the corresponding coefficients in acetone. This shows quite clearly that the solvates formed in the acetone solutions are very much less complex than those formed in the aqueous solutions. Since the ions in acetone have, as we have just seen, a much smaller atmosphere of solvent to

carry with them as they move through the solution than they have in the aqueous solutions, their velocity becomes much greater. These two factors both act in the same direction, *i. e.*, they both tend to increase the ionic velocity, and are quite sufficient to justify the conclusion that the molecular conductivities of potassium sulphocyanate are greater in acetone than they are in water, because of a very great increase in the velocity of the ions in the acetone solutions.

NEGATIVE VISCOSITY COEFFICIENTS.

It has been known for a number of years *that when certain salts are dissolved in water the resulting solutions have a smaller viscosity than the pure water*. Several theories have been proposed to explain this phenomenon. A brief but comprehensive outline of these theories has been given by Jones and Bingham,¹ and a mere reference to the literature will suffice in this connection. Euler² employed the "electrostriction theory" of Drude and Nernst³ as a probable explanation of the negative viscosities; but it was later shown by Wagner⁴ that this theory is incorrect, because the viscosity of a solvent may be lowered by the addition of certain non-electrolytes. Dunstan,⁵ Blanchard,⁶ Varenne and Godefroy,⁷ Thorpe and Rodger, and Traube⁸ all seem to attribute the abnormalities in viscosity to the presence of hydrates. The hydrate work of Jones and his co-workers has clearly shown that potassium chloride and similar salts are but little hydrated, even in dilute solutions; and since potassium chloride is one of the salts which produces a marked negative viscosity when dissolved in water, it is very difficult to see how hydrates could enter into the question of negative viscosity to any appreciable extent. Wagner⁹ has made a study of the effect on the viscosity of water of about forty-five inorganic salts. From his data we find that the only salts which produce negative viscosity are the salts of cæsium, rubidium, potassium, and thallium (in the thallos conditions), viz, cæsium chloride, rubidium chloride, potassium chloride, potassium nitrate, and thallos nitrate. All potassium salts do not have this property of diminishing the viscosity of water. Potassium sulphate, potassium ferrocyanide, potassium ferricyanide, and potassium chromate, all give positive viscosity coefficients. But this is not at all surprising, since, as has already been mentioned, it was clearly shown that the viscosity of a salt solution is an additive function of the metallic and the non-metallic ions of the dissolved salt. In other words, the cations and anions seem to work counter to each other in some cases, such as potassium sul-

¹ Loc. cit.

² Ztschr. phys. Chem., **25**, 536 (1898).

³ Ibid., **15**, 79 (1894).

⁴ Ibid., **46**, 867 (1903).

⁵ Ibid., **49**, 590 (1904).

⁶ Journ. Amer. Chem. Soc., **26**, 1315 (1904).

⁷ Compt. rend., **137**, 992 (1903); **138**, 990 (1904).

⁸ Phil. Trans., **185A**, 307 (1894).

⁹ Ztschr. phys. Chem., **5**, 31 (1890).

phate, where the SO_4 ions tend to produce a positive viscosity coefficient to such a great extent as to overcome entirely the negative effect of the potassium ion; and the resultant action is the production of a positive viscosity coefficient by potassium sulphate when dissolved in water. The above facts show very clearly that there is some close connection between the physical properties of caesium rubidium, and potassium and the negative viscosity phenomena. In discussing viscosity in general, Thorpe and Rodger¹ state that "Viscosity is, no doubt, the net result of at least two distinct causes. When a liquid flows, during the actual collision or contact of the molecules, a true, friction-like force will be called into play, opposing the movement. But in addition to this cause, even after the actual collision, molecular attractions will exercise a resistance to forces which tend to move one molecule past another."

Our study of viscosity has led us to the same conclusion as that arrived at by Thorpe and Rodger, viz, that viscosity phenomena are largely a function of the frictional surfaces of the ions, molecules, and molecular aggregates in any given solution. If now by any possible means the total frictional surface should be decreased, then the viscosity of the solution would also be decreased. Suppose that into a solvent containing molecules with comparatively small molecular volume we bring a salt which yields particles having relatively large atomic or ionic volumes. The larger particles of the dissolved substance would be distributed among the smaller molecules of the solvent, and these smaller molecules, instead of coming in contact with each other so frequently, would come in contact with the larger salt particles, and thus the total frictional surface involved would be decreased and, consequently, the viscosity of the solution would also be decreased. In other words, the effect of bringing those salts whose ions have large atomic volumes into pure water, would be the same as if some of the molecules of the water had combined into larger spheres, and thus caused a diminution in the total frictional surface. Since most salts do not produce such an effect on water, we must assume that their atomic volumes are too small, and that only the salts of those metals having very large atomic volumes could produce a diminution in the viscosity of water. The explanation proposed above for the negative viscosity phenomena can then be easily tested by a glance at the atomic volume curves of the elements. When this test is applied, we find that caesium, rubidium, and potassium stand at the *very maxima of the atomic volume curve, and that none of the other elements have anything like as large atomic volumes as the three elements just named*. Furthermore, if our hypothesis is correct, then *that ion which has the largest atomic volume should produce the greatest decrease in the viscosity of water, and the ion having the next smaller atomic volume should produce smaller decrease in the viscosity of water*. Here again we find that our theory

¹ Loc. cit.

is in perfect accord with the facts, as far as they are recorded. According to the work of Wagner,¹ caesium chloride in normal solutions lowers the value of η^2 from 1.0000 to 0.9775; rubidium chloride under the same conditions lowers the viscosity of water from 1.0000 to 0.9846; and potassium chloride in normal solution lowers the viscosity of water from 1.0000 to 0.9872. The atomic volume curve shows that caesium has the largest atomic volume (about 74), rubidium is next in order (about 57), and potassium has the smallest atomic volume (about 47) of this group of metals which produce the negative viscosity in water.

It is worth noting that the difference between the values of η for caesium chloride and rubidium chloride is much greater than the difference between rubidium chloride and potassium chloride. This is in keeping with the relative atomic volumes of the three elements. The difference between the atomic volumes of rubidium and caesium is much greater than the difference between the atomic volumes of rubidium and potassium.

If we extend the above conception to other cations with large atomic volumes, but with much smaller atomic volumes than the alkalis, we shall find that it holds satisfactorily. Take calcium, strontium, and barium, which, of all cations, have the next larger atomic volumes, and compare their chlorides with respect to the values of η ; we have, for normal solutions:

Calcium chloride	η 1.1563
Strontium chloride	1.1411
Barium chloride	1.1228

These values are all positive, as we should expect them to be, but their order is exactly the *reverse of the atomic volumes*, just as we should expect.

Chlorides with cations of smaller atomic volumes have values of η much larger than the above. This will be seen from the following table, where all the values of η refer to normal solutions. In the same table are given the approximate atomic volumes of the cations of the salt.

	At. vol.	η
Magnesium chloride . . .	14	1.2015
Cupric chloride	8	1.2050
Manganous chloride . . .	7	1.2089
Nickel chloride	7	1.2055
Cobalt chloride	7	1.2041

It is obvious that for the atomic volumes of the same order of magnitude, the values of η are of the same order of magnitude; and, in general, the larger

¹ Ztschr. phys. Chem., 5, 35 (1890).

² η , the time of flow of water through the viscometer, is taken as unity.

the atomic volume the smaller the value of η , just as we should anticipate in terms of our hypothesis.

The small values of η for cadmium and mercury are due to the fact that the salts of these metals are only slightly dissociated.

Thallium seems at first glance to present an exception, but it is to be remembered that it is the thallos salt which produces the negative viscosity. The atomic volume curve deals with thallium in the thallic condition, and, consequently, thallium can not at present be considered as a test of our hypothesis.

CONCLUSIONS.

(1) We have measured the conductivities of various concentrations of copper chloride in water, methyl alcohol, ethyl alcohol, and in binary mixtures of these solvents. We have also measured the conductivities of various concentrations of potassium sulphocyanate in water, methyl alcohol, ethyl alcohol, acetone, and in binary mixtures of these solvents.

(2) Further, we have measured the fluidities of the above-named solvents and mixtures of these with one another; also the fluidities of solutions of potassium sulphocyanate in these solvents.

(3) A minimum in conductivity was observed in certain of the mixtures of the solvents. The hypothesis of Jones and Lindsay as substantiated by the work of Jones and Murray has been discussed.

(4) It has been shown that in nearly all cases where actual minima do not occur, there is nevertheless a decided dropping of the conductivity curves below the values as calculated from the rule of averages; and that this drop is most pronounced in the 25 per cent and 50 per cent mixtures, which are the points at which the actual minima usually occur. It has also been shown that these cases of dropping of the values below the values calculated from the rule of averages constitute cases of virtual minima, and we have extended the hypothesis of Jones and Lindsay to such cases, and have shown that the hypothesis when applied to the problem of conductivity in mixed solvents is perfectly general.

(5) A minimum in the fluidity curves of the above solvents has been observed, and the cause of this minimum has been explained as follows: It has been shown that viscosity and fluidity are largely frictional phenomena; and that since when two associated liquids are mixed they mutually decrease the association of one another, they thus increase the number of molecules present, and, consequently, increase the total frictional surface, thus causing an increase in viscosity (or decrease in fluidity). Further, it has been shown that the point of maximum viscosity is the point where the effect of the solvents upon each other is greatest; and, consequently, is the point at which we have the greatest number of simple molecules present. This has been

shown to be an additional proof of the hypothesis of Jones and Lindsay to account for the minima in conductivity.

(6) A maximum in conductivity has been observed similar to, and in the same solvents as the maxima in conductivity found by Jones and Bingham. The explanation offered by them to account for these maxima has been discussed, and it has been shown that their explanation only partly accounts for the facts. We have offered an additional explanation which is as follows: We have seen that at these maximum points of conductivity, the fluidity of the mixed solvent is also a maximum. We have shown that this maximum fluidity is due primarily to an increase in the size of the molecules of the solvents. We have shown further that this enlarging of the molecular spheres can not be due to increased association of either of the pure solvents, and must be due to a molecular aggregation of the solvents with one another. The conditions for such a molecular aggregation are probably most favorable in the particular mixtures in which the maximum fluidities occur. Since the fluidity of the solvent is increased, the velocity of the ions is increased; and, consequently, we conclude that the maxima in conductivity are dependent upon two factors—the change in the size of the ionic spheres, and the change in the fluidity of the solvent.

(7) We have shown that the dissociating action of any given solvent towards electrolytes is not dependent solely upon the physical properties of the solvent, but is also dependent upon the nature of the dissolved salt. That this is true is seen from the fact that although ternary electrolytes, in general, have a higher molecular conductivity when dissolved in water than binary electrolytes, yet when dissolved in methyl alcohol, or ethyl alcohol, or acetone, the conditions are exactly reversed; and the binary electrolytes show the greater molecular conductivities in these solvents. This is probably due to the breaking down of ternary electrolytes into their simplest ions in some solvents, while in other solvents they yield only two ions; whereas the binary electrolytes are dissociated in the same manner in all solvents.

(8) We have observed that the temperature coefficients of conductivity in the 25 per cent mixtures of the organic solvents with water are a maximum. This is probably due to the formation of more complex solvates between the dissolved substance and solvents in these particular mixtures than in any other mixtures of these solvents. These are the mixtures in which we have the simplest solvent molecules present, and, consequently, the most favorable conditions for the formation of solvates.

(9) We have observed a much greater molecular conductivity of potassium sulphocyanate in solutions in acetone than in aqueous solutions. We have shown that this might be due to either of two causes: (1) A greater degree of dissociation in acetone than in water. This view is untenable on account of the small association and dielectric constant of acetone as compared with that

of water. (2) A much greater velocity of the ions in acetone than in water. This has been demonstrated to be correct, since the fluidity of acetone is much greater than that of water, and especially because the solvates formed in water are much more complex than those in acetone, as is shown by the great difference in the temperature coefficients of conductivity. These are about ten times as great in aqueous solutions as they are in acetone solutions.

(10) A *negative coefficient of viscosity* has been found for potassium sulphocyanate in aqueous solution, and we have offered the following explanation to account for it, after having called attention to the fact that all previously offered explanations are inadequate.

From the experimental data recorded by Wagner we find that caesium, rubidium, and potassium are practically the only ions that produce the negative viscosity in aqueous solution. We have further pointed out that all potassium salts do not give a negative viscosity, and that this is due to the fact that viscosity is an additive function of both the ions involved; and that in some cases the action of the anion, tending to produce a positive viscosity, is sufficient to overcome the action of the potassium ion which tends to produce a negative viscosity in aqueous solution. We have pointed out the fact that the total frictional surface in a liquid would be diminished by the introduction into that liquid of a substance which gives ions with atomic volumes much larger than the molecular volumes of the molecules of the liquid itself; and we find that such is probably the case when caesium, rubidium, and potassium salts are dissolved in water.

We have tested our suggestion by reference to the atomic volume curve of the elements as drawn by Lothar Meyer, which, as is well known, shows that potassium, rubidium, and caesium have by far the largest atomic volumes of any of the elements. We have still further tested our hypothesis by showing that the amount of negative viscosity produced by the chlorides of these three elements is in the same order as their relative atomic volumes.

BIOGRAPHY.

The author of this dissertation, William Reed Veazey, was born in Chase City, Virginia, on December 29, 1883. His preparatory training was received in the public schools of Chase City, Virginia, and of New Wilmington, Pennsylvania, and in the Preparatory Department of Westminster College, New Wilmington, Pennsylvania. He entered Westminster College in 1899, where he received the degree of A.B. in 1903. During his senior year he was assistant in chemistry at Westminster College.

In October, 1903, he entered the Johns Hopkins University as a graduate student in chemistry, with physical chemistry and mathematics as subordinate subjects. During the year 1904-1905 he occupied the position of instructor in chemistry in the University of Oregon. He returned to the Johns Hopkins University in October, 1905, where he devoted most of his time to physical chemistry, and his dissertation was prepared in this field. In the year 1905-1906 he was one of the laboratory assistants to Dr. Gilpin, and in the year 1906-1907 he held a university scholarship at the university.

